RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XI NUMBER 2

April, 1938

Published under the Auspices of the
RUBBER DIVISION *of the* AMERICAN CHEMICAL SOCIETY

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues ($2.00) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division upon payment of $4.00 per year to the Treasurer of the Rubber Division, and thus receive Rubber Chemistry and Technology.

(3) Companies and Libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $6.00 per year.

To these charges of $2.00, $4.00, and $6.00, respectively, per year, extra postage must be added at the rate of $.20 per year for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given Rubber Chemistry and Technology.

Rubber Division Activities

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Rubber Technology Conference

To Be Held in London under the Auspices of the Institution of the Rubber Industry, May 23–25, 1938

The scope and aims of the Conference have been described in the January, 1938, issue of RUBBER CHEMISTRY AND TECHNOLOGY.

The Conference Committee has announced that the following papers have been accepted. Numerous others have been promised but not received.

The pendulum method of resilience testing. F. B. Jones and W. H. Pearce.

The testing and control of quality of latex. E. A. Murphy.

The mastication of rubber—Notes on some of the oxidation processes involved. W. F. Busse.

Dielectric losses in rubber. C. Zwikker.

The crystallization of rubber and its technical durability. H. Mark.

Composition and colloidal properties of balata latex. A. R. Kemp.

Modifications of colloidal properties of rubber latex and technological applications. C. M. Blow.

Artificial materials possessing properties of rubber. R. Lepsius.

Preparation and properties of halogenated derivatives of rubber from latex. H. C. Baker.

Rubber plastics. H. Barron.

Methods of evaluating durability of rubber thread. J. P. Griffiths.

Testing and properties of rubber from latex. G. W. Usherwood.

Application of thermodynamics to the chemistry of rubber. Norman Bekkedahl.

Values of the physical constants of rubber. Lawrence A. Wood.

L'oxydabilité considerée comme test d'état du caoutchouc. C. Dufraisse.

Applications de la mesure de l'oxydabilité. C. Dufraisse and J. Le Bras.

Cyclised rubber, particularly boron fluoride transformations. H. P. Stevens and C. J. Miller.

Researches into the nature and properties of ebonite. B. D. Porritt.

Comparison of accelerated and natural aging under various conditions. J. R. Scott.

Color measurement and its applications in the rubber industry. W. H. Willott.

Purified latex and rubber. R. J. Noble.

En vue d'étudier la constitution des latex et leurs rapports avec la vie des végétaux. E. De Wildeman.

Plasticity and color of sheet rubber. J. D. Hastings.

Fatigue in rubber. Part II. New method of measuring the effect of fatigue on the elastic properties of rubber. W. J. S. Naunton and J. R. S. Waring.

Effect of aging on the water absorption of vulcanized rubber. J. A. Robertson.

Application of high-frequency current in the rubber industry. H. Leduc.

Die Entwicklung der Regeneriertechnik im Verlauf von 100 Jahren. P. Alexander.

Mechanism of oxidation of rubber and its bearing on accelerated aging tests. L. B. Morgan and W. J. S. Naunton.

Some problems in relation to the production of latex and rubber on plantations. B. J. Eaton.

Heat of reaction and other phenomena of gas vulcanization. A. M. Malcolm, F. H. Cotton, and R. Buckingham.

Effect of tension on the chemical activities of rubber. D. Banerjee, F. H. Cotton, and R. W. West.

Change in unsaturation of rubber during vulcanization. D. Banerjee, F. H. Cotton, and R. W. West.

An investigation of the performance of flat and V-type transmission belts. S. A. Brazier.

Einige Probleme aus der Kabelindustrie. F. Lion.

Ketone-amine products as rubber antioxidants. R. L. Sibley.

Direct determination of oxygen in rubber. H. I. Cramer, I. J. Sjothun, and L. E. Oneacre.

A relationship between the critical oxidation potentials and antioxidant activity of rubber antioxidants. E. B. Babcock.

Studies of the electrokinetic behavior of latices. E. A. Hauser.

Practical significance of some recent observations in relation to latex. D. Spence.

The testing of rubber at low temperatures. J. H. Carrington.

Vulcanizing properties of rubber carbons. W. B. Wiegand and J. W. Snyder.

Kautschukelastizität und Gaselastizität. H. Mark.

Situation of rubber sales territories in Scandinavia. Autogummi-Forhandler-Foreningen.

Use of rubber tires on agricultural implements in France. P. Petithuguenin.

Some problems in the use of rubber threads in textiles. W. Davis.

Some aspects of polymerization in rubber-like compounds. E. K. Rideal.

Tackiness of raw rubber. O. De Vries.

Measurement of the absorption of oxygen by rubber in air. A. G. Milligan and J. E. Shaw.

Special uses of rubber in high-voltage underground cable manufacture. A. M. Jamey.

Personal observations on the preparation of rubber on plantations in relation to its variability. V. Cayla.

Additional promises of papers have been received from:

C. R. Boggs, G. Bruni, G. E. Coombs, J. R. M. Duncan, Établissements Hutchinson, H. L. Fisher, J. G. Fol, T. L. Garner, Gesellschaft für Technischen Fortschritt, H. Heering, M. M. Heywood, F. Kirchhof, W. L. Semon, P. Stöcklin, D. F. Twiss, Van der Wyk, A. van Rossem, G. S. Whitby, Ira Williams, and C. G. Williams.

The following organizations have agreed to coöperate. (The official delegates are shown in parentheses.)

Admiralty, Department of Scientific Research and Experiment (A. G. Milligan,

J. E. Shaw); American Chemical Society, Rubber Division (A. R. Kemp); Association Belge des Techniciens du Caoutchouc et Autres Matières Plastiques (A. R. Matthis); Association Colonies-Sciences (Paris) (Victor Cayla); Association Française de Normalisation; Association of British Chemical Manufacturers (J. Davidson Pratt); Aston Technical College, Rubber Department (D. Dudgeon Stockley); British Association of Research for the Cocoa, Chocolate, Sugar Confectionery, and Jam Trades (L. E. Campbell); British Boot, Shoe, and Allied Trades Research Association (H. Bradley); British Cotton Industry Research Association (Sir Robert Pickard); British Electrical and Allied Industries Research Association (H. F. Church); British Food Manufacturers' Research Association (L. E. Campbell); British Leather Manufacturers' Research Association; British Rubber Producers' Research Association (G. E. Coombs); British Scientific Instrument Research Association (H. Fry); British Standards Institution (C. le Maistre); Cable Makers' Association (A. E. Tanner); Ceylon Estates Proprietary Association (H. F. Parfitt); Chemical Defence Research Department (N. K. Johnson); Chemical Research Institute (Warsaw); Chemical Society (B. D. Porritt); Department of the War Department Chemist (B. C. James); Government Laboratory (F. S. Aumonier); Imperial Institute (Sir Harry Lindsay); India Rubber Manufacturers' Association (Alexander Johnston); Institute of Chemistry of Great Britain and Ireland (D. F. Twiss); Institute of Physics (W. Makower); Institut Français du Caoutchouc (C. Dufraisse); Institution of Automobile Engineers (H. Kerr-Thomas); Institution of Automobile Engineers, Research Dept.; Institution of Chemical Engineers (T. L. Garner); Institution of Electrical Engineers (P. Dunsheath); Institution of Gas Engineers (C. R. Austen); Institution of Mechanical Engineers (H. C. Young); Institution of Petroleum Technologists (W. E. Gooday, F. B. Thole); London Advisory Committee for Rubber Research (Ceylon and Malaya) (P. J. Burgess); London Shellac Research Bureau (A. J. Gibson); National Research Council of Canada (G. Stafford Whitby); Netherlands Government Rubber Institute (A. van Rossem); Newton Heath Technical School, Rubber Department (E. H. Wallace); Northern Polytechnic, Rubber Department (T. J. Drakeley); Office Technique des Planteurs d'Indochine (Victor Cayla); Post Office Research Department (D. W. Glover, R. Lynch, E. V. Walker); Printing and Allied Trades Research Association (C. Ockrent); Research Association of British Rubber Manufacturers (Sir Harold Hartley); Royal Institution of Great Britain (W. A. Caspari); Royal Society of Arts (Sir Walrond Sinclair); Rubber Growers' Association (A. P. Hadow); Rubber Research Institute of Malaya; Rubber Research Scheme (Ceylon) (M. W. Philpott); Rubber-Stichting (Rubber Foundation, Amsterdam) (J. G. Fol); Rubber Trade Association of London (J. E. Nathan); Science Museum (A. Barclay); Society of Chemical Industry, Ottawa Section (G. Stafford Whitby); Society of Chemical Industry, Plastics Group (W. J. S. Naunton, H. Barron); Society of Dyers and Colourists (J. Blair); Society of Public Analysts and other Analytical Chemists (P. Schidrowitz); Stow College, Rubber Department (J. R. M. Duncan); Syndicat Professionnel des Fabricants de Fils et Cables Electriques (M. Riedinger); Textile Institute; Union Nationale des Syndicats des Tissus Elastiques (Paris) (J. B. Lefebvre); United States Department of Commerce, Bureau of Standards (Norman Bekkedahl, Lawrence A. Wood); U. S. Department of Commerce, Bureau of Foreign and Domestic Commerce (Warren S. Lockwood); Verband der Kautschuk und Asbestwarenindustrie (Vienna) (H. Kassner); Verband Deutscher Elektrotechniker (R. Lepsius); War Office Research Department; Wool Industries Research Association (C. M. Blow).

The Meeting of the Rubber Division in Detroit, Michigan, March 28–29, 1938

The meeting was held in the Crystal Room of the Book-Cadillac Hotel, with approximately three hundred in attendance.

The meeting in the forenoon of March 28 was devoted to a report of the Crude Rubber Committee, which was read by R. H. Gerke, Chairman of the Crude Rubber Committee.

This was followed by a general discussion by the membership on ways and means of obtaining more nearly uniform rubber.

The following program was presented in the afternoon of March 28:

1. Oxygen pressure aging. I. Improved equipment. By L. M. Freeman.
2. Statistical theory of the Elasticity of Natural and Synthetic Rubber. By Eugene Guth.
3. Effect of ternary mixtures of zinc oxide, channel black and clay on the physical properties. By J. P. Marcelo, O. D. Cole, and H. I. Cramer.
4. The chemistry of soft rubber vulcanization. VI. Reversion and non-reversion in low sulfur compounds. By B. S. Garvey, Jr., and D. B. Forman.
5. Extraction of water-soluble accelerators in water cure. By J. W. MacKay.
6. The structure of rubber in solution. II. Colloidal effects of precipitants. By S. D. Gehman and J. E. Field.
7. Processing characteristics of rubber compounds as affected by pigment particle size and surface. By A. H. Nellen and C. E. Barnett.
8. Flocculation of pigment in carbon black-rubber mixtures. By C. R. Park and Paul P. McLellan.

The Rubber Division banquet was held on the evening of March 28 in the ballroom of the Book-Cadillac Hotel, with three hundred and fifty in attendance.

The Banquet Committee is to be congratulated on the fine dinner and excellent entertainment which they provided.

The Rubber Division also wishes to thank the following companies for the financial support given the Committee to make the excellent program possible:

American Zinc Sales Co.
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United Carbon Co.
U. S. Rubber Reclaiming Co.
R. T. Vanderbilt Co.
C. K. Williams & Co.
Wishnick-Tumpeer, Inc.
Xylos Rubber Co.

The Rubber Division also wishes to thank the Detroit Rubber Group for their efforts in making this entire meeting a success.

Tuesday morning, March 29, was devoted to a discussion on the use of rubber in the automotive industry. The speakers were:

1. H. T. Wollson, Chrysler Corporation
2. R. H. Plumb, Graham-Paige Motor Company
3. J. D. Morron, U. S. Rubber Products Company
4. H. A. Winkelmann, Dryden Rubber Company
5. A. W. Oakleaf, U. S. Rubber Products Company

On Tuesday afternoon, the following plant visitations were made:

1. Plymouth Motor Division, Chrysler Corporation—Assembly Line
2. Ford Motor Company—Steel Mill
3. Research Laboratories, General Motors Corporation—Demonstrations
4. U. S. Rubber Products, Inc.—Tire and Automotive Division

C. W. CHRISTENSEN, *Secretary-Treasurer*

New Books and Other Publications

Latex and Rubber Derivatives and Their Industrial Applications. Volume II and III. Frederick Marchionna. The Rubber Age, 250 West 57th St., New York, N. Y., 1937. Cloth, 6 × 9 in. 1670 pp. Comprehensively indexed. Price: Volumes II and III, $20.00 (Not sold separately).

In the first volume of this book, which appeared in 1933, the author reviewed all the publications on latex up to July, 1932. Every rubber technologist who has used this work is acquainted with the exact and ready information found therein.

The two new volumes represent a supplement devoted to new work published since the appearance of the first volume. The same general plan, found to be successful, has been maintained, but the scope of the work has been enlarged to include derivatives of rubber. Many of the chapters have introductions by specially qualified authors.

For the period of about four and one-half years covered by this work there are 2932 abstracts on latex and 941 on rubber derivatives. These abstracts cover all American, English, French, and German patents and all important articles published throughout the world.

Professor Bruni, who wrote the preface, said with reason that there are very few, if any, fields of technical knowledge and industrial applications having a reference work as reliable and as complete as that of latex.

A list of chapters follows, with the names of the authors who have written introductions: **Volume II. Part 1—Latex and Its Industrial Applications.** (1) Latex and Its Properties; (2) Conditioning of Latex (J. McGavack); (3) Vulcanized Latex and Vulcanization Processes (P. Schidrowitz); (4) Compounding and Compounded Latex (P. Schidrowitz); (5) Depositing Latex Processes and Dipped Articles (C. L. Beal); (6) Rubber Threads and Filaments Manufacture (D. F. Twiss); (7) Textile Fabric Manufacture; (8) Paper and Artificial Leather Manufacture (G. A. Richter and M. O. Schur); (9) Coating and Impregnation (A. Szegvari); (10) Electrical Insulation; (11) Porous Rubber Products (D. F. Twiss); (12) Floor and Road Coverings; (13) Shoe Manufacture. **Volume III.** (14) Rubber Powders; (15) Miscellaneous Processes and Products; (16) Artificial Latex and Mixed Dispersions; (17) Electrodisposition of Rubber (C. L. Beal). **Part 2—Rubber Derivatives and Their Industrial Applications.** An introductory article by H. L. Fisher on the Composition and Structure of the Rubber Hydrocarbon. (18) Oxidized Rubber; (19) Hydrogenated Rubber; (20) Halogenated Rubber Products; (21) Cyclized Rubber (L. B. Sebrell and E. J. Morris); (22) Condensation Products of Rubber.

The work concludes with indices which refer to the numbers assigned to the abstracts. This enables one to find an abstract immediately (much sooner than if the reference were merely to the page number) in any four sections: (1) Author Index, (2) Patent Index, (3) Patent Index by number, (4) Subject Index.

These three volumes represent an authoritative work of great value to all rubber engineers and technologists The author has rendered a very great service to those interested in rubber by this publication of his painstaking and extensive work. [From *Le Caoutchouc & la gutta-percha.*]

Recueil des Communications. Published by Revue générale du caoutchouc, 19 Boulevard Malesherbes, Paris, France. $8^1/_2 \times 10^1/_2$ in. 212 pp. 100 Francs (approximately $4.50).

All of the 38 papers delivered at the recent International Rubber Congress held in Paris on June 28–30, 1937, appear in this publication. In addition, the welcoming speeches by the executives of the various organizations sponsoring the Congress, and a complete list of technologists visiting the Congress, divided by nationalities, are included. Of the papers, 11 are devoted to the properties and applications of latex, 19 to the properties and applications of rubber, and 8 to synthetic rubbers and chemical derivatives of rubber. This book serves a very useful purpose, and it is to be regretted that it appears only in French. [From *The Rubber Age* of New York.]

Modern Rubber Chemistry. Harry Barron. Chemical Publishing Co. of N. Y., Inc., 148 Lafayette St., New York, N. Y., 1938. 342 pp. Price, $7.50.

The author of this book has perpetrated many blunders, the least of which is probably the choice of the term "Modern" in its title. Unfortunately, the rest of the title is even less justifiable. Thus, on the subject of rubber, page 223, we find isoprene graphically formulated with molecules of 4 carbon atoms, from 4 of which in chain are derived molecules labeled "Rubber" having 5 conventional double bonds unsymmetrically distributed among 16 carbon atoms. This strain on one's credulity is, however, intensified by the discovery of the weird auxiliary linkages which are invoked to give the appearance of valence 6 on one carbon atom. The repetition of this weird formula, which is certainly not that of rubber, is found in the formulation of soft vulcanized rubber. Logically, it is next in order to examine the author's conception of chemistry, the third term in the title, since in his preface, page 7, "chemistry as a whole suffers from too much unexplained jargon." It does not help much to find on page 92, "One of the greatest objections to rubber has been its inflammability. In connection with overcoming this the heat of combustion is a most important piece of information."

None of the chapters up to the fifteenth is free from blunders and inaccuracies. This chapter, on Compounding of Rubber, is fairly well done except for the section on Carbon Black, where for at least the second time, pages 26 and 173, Wiegand is erroneously credited with the discovery of carbon black as a reinforcing agent. However, the citation of credit to Wiegand on page 173 is compromised by the apocryphal "It is now accepted that the first use of carbon black in tyre treads was at Silvertown by Mote in 1906 * * * *. The early use of carbon black in tyre treads has been attributed to Oenslager of accelerator fame." The reader is apparently privileged to choose his own inventor.

The chapter on Accelerators is filled with inaccuracies. Page 187. It was not *p*-aminodiphenylamine, but dimethyl *p*-phenylenediamine which constituted the discovery of Spence. The term "tricarbanilide" is entirely cryptic and erroneous. Page 188. Di-*o*-tolylguanidine is not a delayed-action accelerator as claimed. Reference to dithiocarbamates in the presence of zinc oxide, "metallic radicals began to replace the basic portion," is confusing to the reader. Diphenylguanidine, on page 194, is given the formula for diphenylamine.

A few of the statements which should hardly be allowed to stand unchanged are the failure, page 103, to distinguish between the work of Fisher and Kirchhof, where a real distinction exists; that on page 47, "too much protective colloid renders the rubber somewhat tacky;" the unjustifiable attempt to correlate various aging tests on page 201; the inexcusable confusion on page 206 of classifying ethylenediamine under the type phenylenediamines, and referring to "aromatic diamines such as the tolylamines;" the definition of thixotropy, page 50. Incidentally, the melting point of phenyl-β-naphthylamine, page 207, is wrong. It should be 108° C. instead of 160° C. "Gualeye," appears on pages 15, 30, as a source of rubber.

This text is certainly not needed. If a simple, readable introduction to rubber

chemistry is being sought, it would be far better to recommend Lothar Weber's revision of the excellent text written years ago by his father.

This book employs anthropomorphic concepts in a number of places, naturally not very effectively: page 45, "colloids sympathetic toward water;" page 46, "protein to exert its prerogative of swelling;" on pages 121, 122, and 123, the chemical composition of rubber is explained in terms of "happy children playing in fours" most unfortunately and ineffectually, because the analogy between hands and valency is not at all fetching.

The author has trouble with grammar, particularly with the tenses, and with his bibliography. All told, the reviewer believes this to be a book that is characterized mainly by confusion. [From *Industrial and Engineering Chemistry.*]

The Chemistry and Technology of Rubber Latex. By C. Falconer Flint. London: Chapman & Hall Ltd., 1938. 735 pp. 42s.

In his treatment of this subject, the author (formerly of the Rubber Research Institute of Malaya and now on latex research and development at the Imperial Chemical Industries, Ltd.) has taken serious note of the advice of the King of Hearts, "Begin at the beginning, and go on till you come to the end: then stop." The result is a comprehensive treatise dealing with all aspects of latex technology from plantation control to the manufactured article. A successful attempt has been made to incorporate information of value to all those whose daily work brings them into contact with rubber latex.

The historical section, so often an unnecessary waste of space in a book of this type, has been made valuable by the inclusion of a review of the patent position. Quotations from various authorities are included in a useful guide to the involved situation created by the numerous patents dealing with latex technology.

The compounding of latex and its application to a wide range of manufacturing processes are adequately described, the use of the word "Technology" in the title being more than usually justified by the inclusion of practical details and typical formulas.

The chemical treatment is limited to the requirements of the latex technologist, and is incidental to the main technological theme. This balance is skilfully maintained throughout the book, with the result that processes are explained and their merits discussed without any unnecessary overloading of the purely theoretical side of the subject.

The subject matter is carefully arranged and the book, in spite of its length, is essentially readable. The scope of this work is indicated by the fact that the text contains more than 1300 references to the original literature. It is sometimes convenient to have a list of the abbreviations used in the references, and the author might consider the inclusion of such a list in future editions. Dr. Flint is to be congratulated on the production of a most welcome addition to English technological literature.

The book is well printed on good quality paper and contains 147 illustrations. [From the *Transactions of the Institution of the Rubber Industry.*]

Asphalts and Allied Substances. (4th Edition.) By Herbert Abraham. Published by D. Van Nostrand Co., Inc., 250 Fourth Ave., New York, N. Y. 6 × 9 in. 1515 pp. $12.50.

The first edition of this monumental work was brought out in 1918. Subsequent editions contained revised and additional data. This latest edition contains several new chapters on hitherto untouched subjects, while a special feature is a bibliography embracing more than 900 treatises. The scope of the latest edition may be

more fully appreciated by the fact that there are more than 9000 references to patents and approximately 3000 citations to the general literature. Like previous editions, it presents full particulars about the natural sources or the industrial methods of production for each bituminous substance. Methods of testing and analysis of asphalts, tars, and pitches and their manufactured products are covered. Processes using these materials for producing pavements, roofings, floor coverings, etc., are described. References to the use and manufacture of products made by blending rubber and latex with bituminous substances appear in several places in the book. The book should also prove of interest to rubber chemists because of constant references to compounding materials which are widely used in rubber manufacture as well as in bituminous products. [From *The Rubber Age* of New York.]

The Chemistry of Petroleum Derivatives. Carleton Ellis. Published by Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. 1937. Cloth, 6 × 9 in. 1464 pp. Illustrated. Index. Price, $20.00.

The present volume continues the subject matter of Volume I, published in 1934, on the chemistry of petroleum derivatives, in some cases with additional references to work published prior to that date. The purpose is to form a comprehensive record of the work done in this field. The voluminous character of the book gives an indication of the activity of the petroleum chemist since 1934, and the book contains much recent material of importance on such subjects as the utilization of by-products of refining, polymerization, detonation, nitration, and thermodynamics.

While the book is devoted essentially to the petroleum industry, there is considerable material pertaining to the chemistry of rubber and related materials. One chapter is concerned with the carbon black industry, wherein are discussed the various processes of producing this material, and the physical and chemical properties of the various types of blacks. Also treated in this chapter are industrial applications and the evaluation of carbon blacks. A number of pages deal with the polymerization of butadiene and chloroprene in the production of synthetic rubber. In addition many other references to rubber chemistry are scattered throughout the book. The volume contains a name index and a subject index. [From the *India Rubber World.*]

Index to A. S. T. M. Standards and Tentative Standards. American Society for Testing Materials, 260 S. Broad St., Philadelphia, Penna. 6 × 9 in. 128 pp.

This latest index gives information on all of the 823 A. S. T. M. standards as of January 1, 1938. It is of use to any one wishing to ascertain whether the Society has issued standard specifications, test methods, or definitions covering a particular engineering material or subject, and is of special help in locating standards in volumes where they appear. All items are listed under appropriate key-words according to the subjects. [From *The Rubber Age* of New York.]

A. S. T. M. Standards on Rubber Products. 1937 Edition. American Society for Testing Materials, 260 S. Broad St., Philadelphia, Penna. 238 pp.

This publication, sponsored by Committee D-11 on Rubber Products, presents in convenient form for laboratory use and reference all the 25 standards issued by the A. S. T. M. in this field. There are 15 methods of testing procedure and nine specifications with a proposed specification for rubber insulating blankets. Among the various types of tests covered are tension, hardness, abrasion-resistance, flexing, compression set, accelerated aging, and chemical analysis. Detailed tests

cover wire and cable, rubber hose, and rubber belting. Specification requirements cover fire hose, rubber pump valves, friction tape, rubber insulating tape, various classes of insulated wire and cable, gloves for electrical workers, etc. In addition to standards a bibliography gives sources of information concerning properties and testing of rubber and rubber products. This includes references which are comprehensive, and lists the more important of the recent publications. Copies of this publication can be obtained from A. S. T. M. headquarters at $1.25 per copy. [From the *India Rubber World.*]

A. S. T. M. Standards on Electrical Insulating Materials. 1937 Edition. American Society for Testing Materials, 260 S. Broad St., Philadelphia, Penna. 373 pp.

This edition, prepared by Committee D-9 on Electrical Insulating Materials, includes all the 37 A. S. T. M. specifications and test methods covering the various types of insulating materials. These standards, presented in their latest approved form, are grouped in the following manner: insulating varnishes, paints, lacquers, etc.; molded insulating materials; plates, tubes, and rods; mineral oils; ceramic products (porcelain, glass); solid filling and treating compounds; electrical tests; papers and fabrics; mica products; rubber products and textile materials. Also included are two proposed standards covering tests for neutralization number of petroleum products and specifications for rubber blankets. Besides the standards, this edition presents three interesting discussions on the significance of tests involving dielectric strength, resistivity, and impact. These discussions have been prepared by three prominent technologists. Copies of this publication can be obtained from A. S. T. M. headquarters at $2.00 per copy. [From the *India Rubber World.*]

Handbook of Chemistry and Physics. Twenty-second Edition, 1937. Chas. D. Hodgman, Editor-in-Chief. Published by Chemical Rubber Publishing Co., Cleveland, Ohio. Fabrikoid, $4^1/_4 \times 6^9/_{16}$ in. 2090 pp. Indexed. Price, $6.00.

The most recent issue of this handbook, for 24 years an authoritative reference work in chemistry, physics, mathematics, engineering, and related sciences, contains data prepared by 173 specialists, and includes over 150 pages of new composition. The handbook is conveniently divided into five sections, each section being indicated by an insert of stiff colored paper on which is printed the contents of the section. The divisions follow: 1. Mathematical Tables; 2. Properties and Physical Constants; 3. General Chemical Tables, Specific Gravity Tables, and Properties of Matter; 4. Heat and Hygrometry, Sound, Electricity and Magnetism, and Light; 5. Quantities and Units—Miscellaneous. New and revised data in this edition include material under the following headings: gravimetric factors, preparation of solutions and reagents, transmission of filters, viscosity, relative humidity from wet and dry bulb thermometer, and index of refraction of fused quartz. [From the *India Rubber World.*]

[Reprinted from News Edition, Industrial and Engineering Chemistry, Vol. 15, No. 21, pages 469–470, November 10, 1937.]

Research Coöperation in the Rubber Industry

William C. Geer

624 Highland Road, Ithaca, N. Y.

One of the outstanding observations which one may make of the rubber industry of today is the high degree of technical competition. Research laboratories are large and their members are well trained and resourceful. The achievements of these groups of competing technologists find their way to the public as patented articles or methods and scientific articles in the literature. In the majority of cases the new products or methods are promptly studied by competing laboratories and ways are found to accomplish the same end by means which do not infringe a given patent. Therefore, much of the energy of research is expended merely in the effort to keep pace with competitors.

Because of this price competition and the narrow margin of total profits, there is a constant pressure upon technical groups to apply their energies to the solution of immediate needs. The physical proximity of the laboratories to the factories and the force of competition usually lead these men to appraise new ideas in the light of practicability. Can the trick be turned within one or two years? If not, efforts should be expended in apparently more fruitful fields.

Although these laboratories are manned by brilliant investigators, whose achievements have been notable, there is not enough attention given to forward-looking research. The driving force behind the investigations which led to the achievements usually rated as the five major ones—accelerators, antioxidants, carbon black, the cord tire, and reclaimed rubber—was the desire to attain a quality improvement in rubber. The condition of the rubber industry of 10, 20, or 30 years hence and the probable degree and kind of our knowledge at the end of such periods are not considered as seriously as should be.

These arguments are sustained by an analysis of W. N. Jones' "Annual Survey of American Rubber Chemistry for 1936." Out of 210 literature references 73.3 per cent are to United States patents. Eleven out of sixteen topics are utilitarian in import. Under the three headings of fundamental significance—properties and structure of rubber, synthetic rubber and rubber-like products, and derivatives of rubber—only nineteen papers describe additions to fundamental knowledge.

These figures show how the minds of the research groups are turned towards the practical and immediate problems in larger proportion than to the scientific basis of this field of study. There are still wide gaps in our knowledge of the fundamentals of rubber and, although the rubber molecule is intricate and complex, that fact affords no basis for an argument that rubber research in that direction has attained pretty nearly its peak.

Granted a need and a field for fundamental research, how best may it be conducted in order to attain greatest success and to conserve the interests of all?

To take a broad view, the competition or coöperation as to research or prices among corporations of a given industry is akin to war or peace among nations. It is no longer true that the victor in a war gains from his conquest; nowadays both

sides lose, whatever may be the territorial outcome. So also in domestic affairs. In every phase of our economic, social, and international intercourse the prime need is for coöperation and mutual good-will, if prosperity and happiness are to be achieved.

Those of us who have been associated with rubber for many years have observed the financial losses due to extreme competition between the several units of our industry. Even in the face of remarkable technical advances, the stockholders have not received their just due and the prosperity which should have been outstanding because of these achievements has not been realized.

Some may explain the situation as one inevitable because of law, but I feel that the low profits have been due rather to the human mind. It has been a case of every man for himself and "the devil take the hindmost."

In the light of history, is it not wise to look ahead 10 or 20 years and consider today what may be done to place the industry of tomorrow upon a new basis? Such a different foundation can be achieved only when we have a vast fund of knowledge of the rubber molecule, what it really is, how it acts, and all the transformations which it can undergo. One visualizes a large program, and an expensive one. Apparatus too expensive for the largest present laboratory would be required. Practical, useful, or patentable results may accrue but, because the field is common to all the corporations, it can more economically be attacked as a cooperative enterprise.

It would seem that research coöperation in the rubber industry has, broadly speaking, two objectives. The first is to achieve a warmer coöperation among the units of our industry. Technical men already get together through the medium of the Rubber Division of the American Chemical Society, within which we all meet upon a common ground. Then too, the products of a number of laboratories in the form of accelerators, antioxidants, etc., are available to all. These products, however, have been developed competitively. If we work out our science together, it seems to me just human nature that the force of extreme business competition will be lowered. The second objective is to strive for a new foundation for the industry of the future. My thought of research coöperation extends beyond that of the invention of a new tire, shoe, or hose, to the discovery of fundamentals because of which new articles and methods may be available to the rubber industry.

Coöperative Research Laboratory

Once again, therefore, I suggest the organization of a comprehensive industry laboratory. The idea is simple—namely, a central laboratory not located in the vicinity of any rubber goods factory.

The building should be generous and superlatively well equipped, so that all phases of research work in rubber could be carried on thoroughly and expeditiously. The appropriation for such a building and its equipment certainly could not be a low one. The rubber industry in this country is a billion-dollar business, the volume of its products is very large, nearly every person in this country uses rubber goods, and the program suggested should be upon a commensurate scale.

The personnel should be large enough to accomplish the aim. I am inclined to believe that a number of research chemists and physicists should be transferred from the laboratories of the present rubber companies to this new central one, provided the best results for the stockholders of the industry are to be attained. A question may well be raised as to whether technical men now competing with each other in separate laboratories would work for the industry as a whole and do it gracefully. I personally believe that they would. But I also believe that such a

scheme would not be approved by rubber company executives unless it carried the whole-hearted approval of the present research leaders.

As for the problems to be undertaken by this new laboratory corporation, heavy emphasis should be given to the nature of rubber and its reactions from the point of view of organic and colloid chemistry.

A very considerable study should be made of the physics of rubber. It is astonishing, when one considers the large sums spent for research work, that we know so little today about the physics and engineering of rubber. The support of machinery by rubber to absorb shock and vibration is a somewhat new use. Each such proposed new application must be studied by cut-and-try methods, and rubber is not yet classed as an engineering material. It is not possible for an engineer on the basis of data supplied by the rubber physicist to design a machine support and select the composition, the size, and shape of the rubber article. This field alone will take some years and the generous use of men, materials, and money, but I believe that uses will be found for a volume of rubber over the future to warrant the cost of such a study.

A third field is an investigation of the rubber-bearing plants which may be grown within the territory of the United States. I have never been one to disparage the work started by Thomas A. Edison, and I feel that over a period of years very large returns to the economics of this country may be made through an exhaustive study of rubber-bearing plants.

The matter of machine design and development for the production of present rubber goods more economically or in better quality and the methods for the production of new articles which a central laboratory might create should be left to the individual companies.

To carry out such a plan successfully a new corporation should be formed, the stock of which would be bought and owned by the companies which support it. Any patents to be issued and knowledge which might not be patentable would be owned by the new research corporation and licensed to the owning and supporting companies in proportion to their ownership and support. Royalties could, of course, be received by the company and dividends declared to the stockholders.

Naturally, it would be necessary not alone to support the corporation by the purchase of stock so that the building could be erected, but also to provide annual appropriations over a period of years. At the end of a reasonable period of time the royalties received from patents should be sufficiently large not only to pay the cost of the laboratory but to declare comfortable dividends and enable the supporting companies to avoid drastic price competition and to gain direct profits from this research work.

A board of directors would be required to guide the financial policies. A director of research capable of managing so comprehensive an enterprise from the technical standpoint could be chosen from a number of men able to guide the largest research corporation that the industry might care to develop.

Possible Disadvantages

Suppose now we weigh the plan. What may be brought up against it? The enterprise would be definitely agreed to for not less than 10 years and preferably for 20 years. A very large sum of money would be used up within that period of time.

It might be said that a joint coöperative laboratory would inevitably lead to a slowing down on the part of technical men. Such might be the case. Yet if the management were able and in complete and enthusiastic sympathy with the plan,

the very fact of coöperation should lead to hard work and quick results. A group of men working on a common problem with common interests, provided the group is well balanced, sufficiently large, and ably led, can do much more and do it quicker than smaller groups working independently. Then, too, the distractions due to proximity of practical men would be much less.

The results of the work, if in the form of new articles, might render less pertinent the advertising of the several companies which might use them. However, such a laboratory could not and would not solve the problem of the introduction of a new article into use. The sales departments of the individual companies would have the problem of finding the places where a new article could be used, and the competition then would be that of developing the volume of business for each company.

Another objection may be made that present laboratories might compete with the new one and so the costs of the new enterprise would be added to those of the present laboratories. That is a question of management. If this coöperative enterprise were actually undertaken in the breadth and on the scale which has been suggested, there would be no reason for the present laboratories to engage in fundamental research. The problems and objectives could be segregated.

Some may argue that there is no need to study the intricacies of rubber because we have reached the end of achievement in a fundamental sense, and only detailed articles and methods can be the objectives of any research program. If that should be actually the best wisdom of the rubber industry, there is no place for the coöperative undertaking under discussion. If the future has to do only with the adaptation of present knowledge to particular articles and uses, so elaborate and expensive a program is not advisable.

A question of law might be raised. Is it within the law to form a new corporation supported jointly by present corporations, the results of whose endeavor would be common property? Frankly, I do not know. This idea has not been proposed to any capable legal mind.

Will chemists and other technical men facilitate such a scheme and work wholeheartedly within it, or would it be retarded because of greater personal ambition than may exist in present laboratories? That would depend partly upon the personality of the individual, partly upon the management. It could be offset by a system of rewards for definite creative work. In large laboratories today, many chemists and physicists are found working in perfect harmony. Results are notable, and the companies have been wise in arranging a series of monetary rewards for achievement. There is no reason why in a joint laboratory a similar system should not be developed and undertaken. Transcending these financial interests would be peace of mind, due to freedom from the pressure of competition, and the joy which comes from service and achievements of value to a larger association.

Advantages

The advantages of this research scheme are many.

To the Science of Rubber.—The increase in knowledge without any implications as to its practical applications cannot fail to be of moment. Even if the fundamental knowledge gained should lead to no practical application, leaders would have facts upon which to base plans for the distant future.

To the Industry.—New products would be developed and new methods found which in all probability would change the scope of an already great industry.

To the Nation.—In the rubber field this country would definitely be kept in the forefront of progress. There are many alert, heavily manned, expensively sup-

ported research undertakings in other countries. It seems only the part of wisdom not to permit any foreign nation or people to grow ahead of us in the rubber field.

To the Individual Worker.—To be a part of a broad, large-scale program which joined the best brains of the chemists and physicists of this country could not fail to be stimulating and highly satisfactory.

To the Stockholders.—Such a program would improve the finances of the individual companies and, therefore, of the stockholders. Certainly under the present laws patents may be licensed for use to the individual members of the corporation and reasonable profits assured.

This is the second time that I have recommended coöperative research to the rubber industry. I hope that it may be realized. I am confident that the executives of the industry will take no steps in this direction unless technical leaders approve and urge the plan. So, it is to the chemists and the physicists of the rubber companies, as well as to the executives, that this plan of coöperative research is suggested.

[Translated for Rubber Chemistry and Technology from a hitherto unpublished paper.]

A Manometer for Measuring the Oxidizability of Rubber

Charles Dufraisse

INSTITUT FRANÇAIS DU CAOUTCHOUC, COLLÈGE DE FRANCE, PARIS

In view of the practical interest in a method for measuring directly the rate of oxidation, *i. e.*, the oxidizability of rubber, it has seemed worth while to devise an apparatus with which the technic of making such measurements is so simple that it is within the compass of operators with no particular training. With this in mind the author has been led to construct a new manometer for measuring oxidizability.[1] Before describing the apparatus and its method of operation, however, it is necessary to explain its principles. Later on, it is intended to deal in a more thorough way with the significance of the measurements, with the various causes of errors arising from the nature of the substance studied and the technic employed, and finally with different ways of expressing the results obtained.

Principle of the Method

The property which the method is designed to measure is oxidizability. In theory the simplest way of evaluating this property would be to use as a basis the quantity of oxygen absorbed in unit time per unit mass of substance oxidized. To do this it would be necessary to derive the kinetics of the reaction in order to know at each instant the rate of oxidation.

If this were the sole aim, it would be preferable to operate at a constant pressure and to measure the oxygen absorbed by means of changes in its volume. The manometric method would in that case have the disadvantage of complicated calculations, particularly with the technic employed, for changes in pressure are accompanied by changes in volume.

As a matter of fact, however, the kinetics involved in the autoöxidation of a substance as complex and heterogeneous as rubber has little significance in itself, either from the theoretical or from the practical point of view. Autoöxidation is a reaction the kinetics of which is somewhat vague, even when a pure substance is concerned. Thus in the case of benzaldehyde, an autoöxidizable compound easy to purify, it is still a debatable question whether in the pure state this compound is or is not capable of absorbing oxygen.[2] Under these conditions it is not at all evident how different authors can be expected to obtain concordant data on the kinetics of a substance as ill-defined chemically and physically as rubber.

Very fortunately the chief interest in measuring the oxidizability of rubber does not lie in determining this property in absolute units. Much more useful because of their reproducibility, and therefore of more direct significance, are relative measurements, which are quite satisfactory for comparative purposes. It is possible to avoid all complications and uncertainties by a comparison, under strictly similar conditions, of the oxidation of unit masses which differ in only one respect. In this way a definite idea can be obtained of the character and the extent of the changes which take place in the various parameters, without having to be concerned in any way with absolute measurements of the oxidizability. It is necessary to calculate the data in absolute terms only in exceptional cases and for special purposes.

For these reasons, and because of its experimental simplicity and its precision in making comparative measurements, the manometric method has been adopted.

The Apparatus

Since it was devised with a view to simplifying and hastening operations, a necessary function of the apparatus is to overcome the two chief difficulties in measuring oxidizability: (1) the complete replacement of air by pure oxygen, and (2) measurement of the changes in pressure of this oxygen.

To overcome the first difficulty, the displacement method has been adopted. To this end, the apparatus has been so constructed that it is possible to sweep out with oxygen every part of the receptacle in which the substance is to be oxidized.

For convenience in measuring pressure, the type of manometer selected should conform to certain conditions, *e. g.*, the necessity of avoiding a reaction chamber of so large a capacity that the sensitivity is diminished too much, the necessity of reliable operation, the ability to be flushed by a current of gas, and finally a construction whereby every part can be cleaned easily. The mercury manometer was chosen as the best means of fulfilling these requirements.

Description of the Apparatus

The apparatus is shown schematically in Fig. 1 and photographically in Figs. 4 and 5. In principle, it is made up of a series of reaction tubes or chambers with unoxidizable walls for holding the substance to be oxidized, which are set in an aluminum block heated electrically and serving as a thermostat.

There are eleven of these tubes, one being used for a control sample in a series

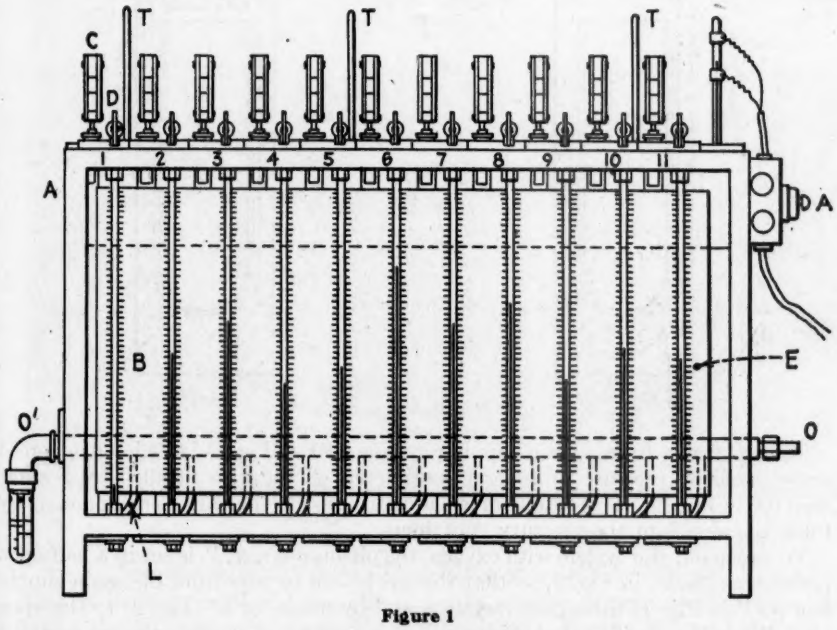

Figure 1

of ten tests. To each reaction chamber is joined laterally near the top, a fine tube connected with the corresponding glass manometric tube. The reaction tubes are closed by means of a stopper of unoxidizable material. As this stopper is an essential part of the apparatus, it seems advisable to describe it in some detail.

It consists of a piston plunger, P, which fits accurately into the inside of the chamber to be sealed, the top edge of which it covers by a groove or channel plugged with an elastic joint (N in Fig. 2). This plunger is grooved along two opposite generatrices which form two narrow passages of unequal lengths, F and F′, the shorter of which is located at the mouth of the side tube. These grooves serve to sweep out the reaction chamber with oxygen, which enters through the side tube, M, from the manometric tube. When the stopper is in a half-open position (Fig. 2), gas enters through M and F in a stream directed towards the bottom of the reaction chamber, which it sweeps out thoroughly before it escapes through the opposite opening, F′.

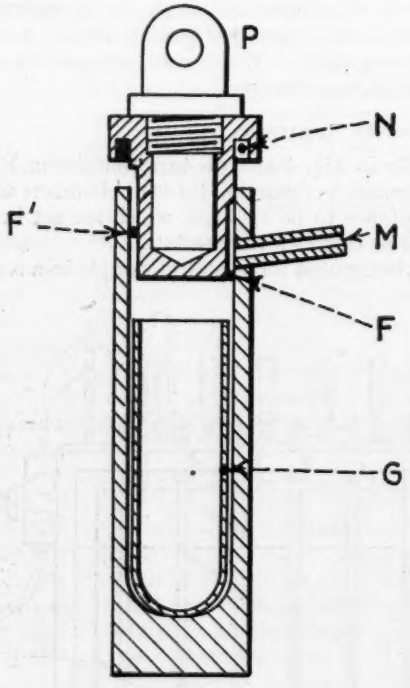

Figure 2

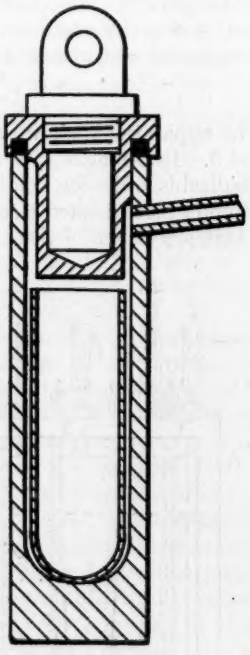

Figure 3

The gas comes from a main supply pipe line (OO′ in Fig. 1) in which it is forced under a slight pressure of several centimeters of water, controlled by a water trap (O′ in Fig. 1). This supply of gas is distributed to the various manometers by tubes opening into the mercury containers.

To sweep out the system with oxygen, the piston plunger, P, is set in a half-open position as shown in Fig. 2, so that the gas is free to pass from the main supply line (OO′ in Fig. 1) through the system, and by means of F′ (Fig. 2) to the open air. When it is decided that this operation is finished, *i. e.*, when the gas escaping through the outlet, F′, sets afire a smouldering match, lever C (Fig. 1), which controls the position of the plunger, is pressed down so that the reaction chamber is sealed tight (Fig. 3). This same movement actuates the plunger in the mercury container, so that the level of the mercury rises and seals the lower end of the manometer. The reaction chamber is then ready for the measurement.

It may be of interest to give a little additional information about the construction of the apparatus.

The material now being used for the reaction tubes is stainless steel, but an apparatus with glass instead of steel is being investigated. Meantime it is advisable to avoid contact with iron of the substance to be oxidized, and to use thin cups (G in Fig. 2) of nickel or other metal, or better still of glass.

For the elastic joint (N in Fig. 2), good results have been obtained with a material of the following composition:

Smoked sheet	100
Sulfur	2
Benzothiazyl disulfide	0.4
Diphenylguanidine	0.4
Stearic acid	1
Aldol-α-naphthylamine	1
Magnesium carbonate	25
Zinc oxide	175

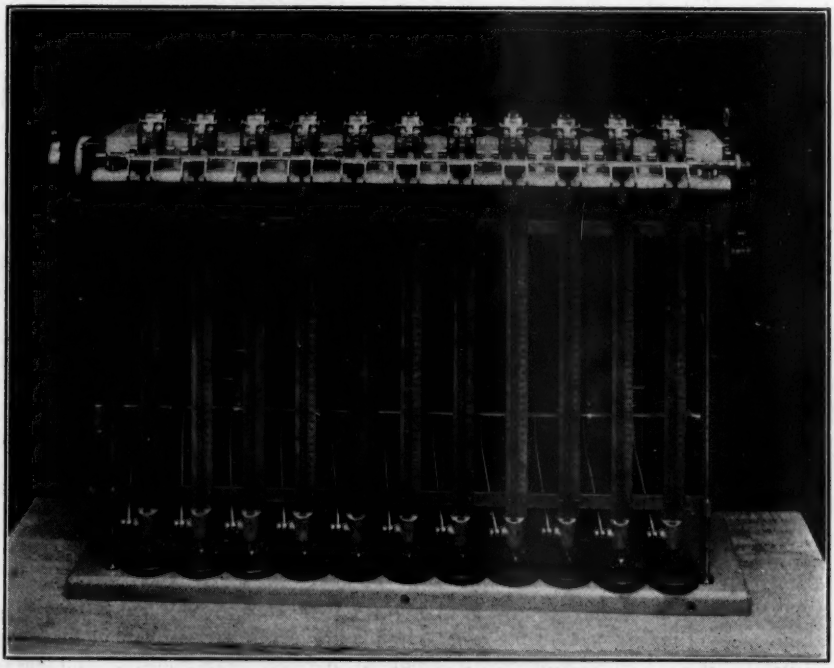

Figure 4

This mixture was milled for 40 min. and vulcanized for 30 min. at 143° C. This particular composition was chosen from a number of mixtures for use as joints, but it has not been accepted finally, for it would be more satisfactory if it did not contain an antioxygenic substance, if it contained less sulfur and if it could be vulcanized more quickly. Nevertheless, this mixture has the advantage of not being readily oxidized, and, in spite of its low rubber content, of behaving satisfactorily under compression. In any case the contact surface of the joints with oxygen is so extremely small that more elastic products could be employed satisfactorily, pro-

vided that a control test without any sample present did not indicate undue oxidizability.

One difficulty in the everyday use of an apparatus of the kind described is the problem of tightening the joints, for there is always the risk either of tightening the joints insufficiently or of squeezing them too tightly. This has been avoided by making the closing an automatic operation by means of springs, which, once adjusted, guarantee the desired pressure at all times.

An important condition in the success of the tests is strict cleanliness of all the walls, and consequently care has been taken that cleaning will involve no difficulties. In the case of the reaction chambers, this is carried out, after withdrawing the stoppers, with wads saturated with suitable solvents. Perfect cleanliness of the interior is assured by examination with a small electric lamp. The side tubes (M in Fig. 2) are cleaned by passing a rod carrying a saturated wad through openings (D in Fig. 1), which connect with the manometric tubes. These openings, which are themselves closed by rubber under compression, serve also for cleaning the manometric tubes. The cleaning wads should be removed from the rods before the latter are withdrawn, otherwise there is danger of the wads becoming lodged in the tubes, which are, in fact, very fine (approximately 2 mm.), with the idea of reducing unnecessary space. The cleaning wad from the side tube is withdrawn through the inside of the reaction chamber, and that from the manometric tube through an opening provided for the purpose at the base of the apparatus in the mercury chamber.

The mercury chamber is arranged in such a way that it conforms to certain necessary conditions. For example, when the stopper of a reaction tube is in open position, mercury should be entirely confined in a side chamber so that there is a clear passage not only in the lower part of the manometer but also in the opening which extends through the wall, so that the manometric tube can be cleaned and changed when necessary.

On the other hand, when the lever closes the reaction chamber, this operation should plunge into the cavity a cylinder, the form, volume, and position of which are calculated for the mercury to seal the manometer and to interrupt the current of gas for flushing the system just a little before the reaction tube is finally closed. In this way danger of return of air is avoided, while at the same time the original level of the mercury is raised to a point where it is visible in the manometer above the metal mounting. Adjusting screws make it possible to control this operation automatically at all times.

Sensitivity

The sensitivity of the apparatus may be regarded as the degree of oxidation which causes the first perceptible rise, ΔH, in the level of the mercury. It depends on two factors: (1) the sensitivity of the measuring apparatus, and (2) the ratio of the capacity of the entire reaction chamber to the volume of oxidizable material.

Theoretically the measuring apparatus can be made very sensitive, like a precise barometer. However, in view of the magnitude of errors due to the nature of the oxidizable substance itself, particularly its heterogeneity, this feature is of no great concern. It would, in fact, be useless for readings to be made with very great accuracy in view of the variability of the chemical reactions involved. It seems reasonable to adhere at all times to an approximation of 1 millimeter, and this will save the expense of an elaborately constructed apparatus, and will avoid complicated corrections.

An effort has been made rather to increase the sensitivity of the test by attention

to the second factor which influences the sensitivity, *i. e.*, the ratio of the volume of oxygen to the mass of substance to be oxidized.

Let V be the total capacity of a reaction tube and its fittings ready for use and v,

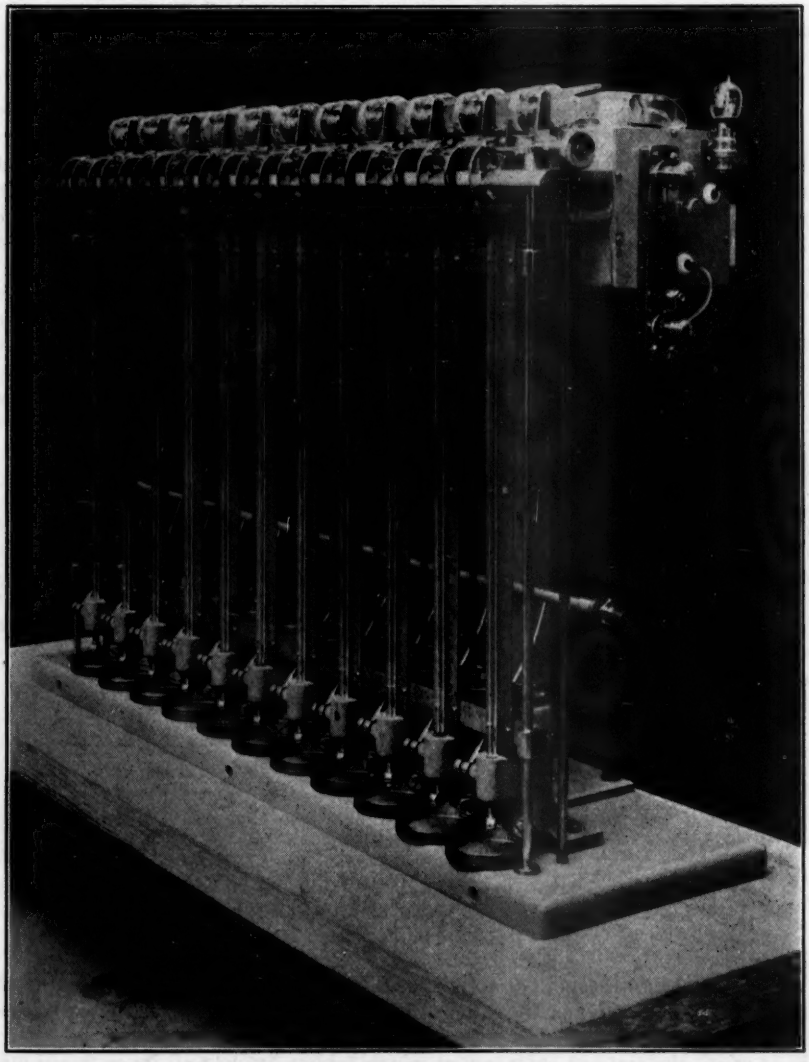

Figure 5

the volume of the substance to be oxidized. Then the change in pressure Δp corresponding to a definite amount of oxidation ΔO is expressed by the equation:

$$\Delta p = p \frac{\Delta V}{V - v - \Delta V}$$

where ΔV represents the volume of oxygen absorbed under the initial conditions. Since this volume of absorbed oxygen is proportional to the quantity of oxidizable substance:

$$\Delta V = kv$$

Hence

$$\Delta p = p \frac{k}{\frac{V}{v} - (1 + k)}$$

It follows that, other things being equal, the greater the quantity of absorbent per unit of total capacity, the more sensitive is the apparatus. This is one reason why the volume of the accessory fittings of the reaction chambers, particularly the volume of the manometer, is to be considered as objectionable capacity, and should be made as small as practicable.[3]

Since on the other hand one of the advantages of the method is that it requires only very small amounts of material, the dimensions of the apparatus have been reduced as much as possible considering the mechanical requirements, particularly in regard to calibration of the manometric tubes.

The dimensions which have finally been adopted are in round figures:

Manometric tube (45 cm. in height)	1.5 cc.
Reaction chamber (closed)	8.0 cc.
Side tube (connecting the manometric tube and reaction chamber)	0.5 cc.

The total volume is then 10 cc., but taking into consideration the volume of the sample[4] and that of the cup containing it, the volume of gas is only around 7 to 8 cc.

If it is assumed that 1 millimeter is the smallest perceptible change in level of the mercury which can be reliably measured, that the volume of gas is 8 cc., that the weight of rubber is 1 gram, and finally that all of this gas is at the temperature chosen for the experiment, the following sensitivities result:

Temperature of the Experiment (° C.)	Height of Mercury in the Manometric Column (Cm.)	Volume of Oxygen Absorbed for a Rise of 1 Mm. (Cc.)	Sensitivity Ratio of the Weight of Oxygen Absorbed to the Weight of Rubber
20	0	0.0129	1.84×10^{-5}
20	40	0.0096	1.37×10^{-5}
40	0	0.0120	1.72×10^{-5}
40	40	0.0090	1.28×10^{-5}
80	0	0.0107	1.53×10^{-5}
80	40	0.0080	1.14×10^{-5}
100	0	0.0101	1.45×10^{-5}
100	40	0.0072	1.03×10^{-5}

What then is the threshold of activity? The calculation which follows, though only rough, gives an idea of the order of magnitude which conforms to the actual phenomena.

First of all, the state of oxidation at which rubber has lost all its ordinary mechanical properties may be assumed to be not far from 1 per cent. It may also be assumed that this degradation is proportional to the percentage of oxygen absorbed.

On the other hand, if the first indications of oxido-aging are to be judged by changes in mechanical properties, it is advisable to regard as significant only changes of at least 20 per cent, because of ordinary deviations in this particular

kind of measurement. In terms of the corresponding state of oxidation, this change in mechanical properties represents a degree of oxidation of 0.2 per cent.

Now, the threshold of sensitivity which has been calculated above for the manometric method is of the order of 0.002 per cent, in other words, a sensitivity no greater than one-hundredth part of the degree of oxidation which can be detected with certainty by changes in mechanical properties.

Then again it should not be forgotten that this threshold is not the theoretical limit of sensitivity of the test, but only a consequence of the fact that the apparatus has been constructed with a view to practical utility, with a sensitivity of 1 millimeter in reading changes in levels of the mercury columns. In principle this

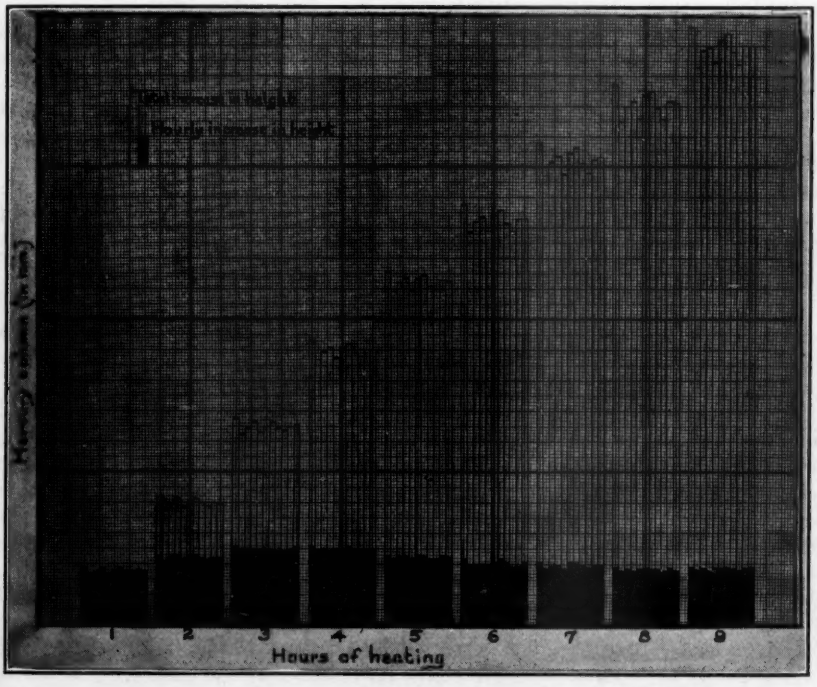

Figure 6—Checking of the Apparatus with Eleven Samples of the Same Vulcanizate
(Total ascents and hourly ascents of the mercury in the eleven tubes for times of heating from 1 to 9 hours)

sensitivity can be readily increased, but little advantage would be gained because of the variations inherent in the reaction itself.

Precision

In estimating the precision of the method, it is necessary to distinguish between measurements which are comparative and those which are not. If the aim is to obtain values of the oxidizability in absolute terms, the absolute values of various factors, such as weights, volumes, temperatures, and pressures, must also be known. In this case it is necessary to measure the weight and volume of the substance to be oxidized, the volume of each part of the system which is not at the same temperature

as the rest of the system, the temperature of each of these parts, and finally the external and internal pressures.

The temperature of the side tube connecting the reaction chamber with the manometer is uncertain because its temperature is merely somewhere between that of the thermostat and that of the outside air. Incidentally, this is another reason for reducing the capacity of the accessory fittings and outside of the thermostat, and therefore of minimizing the diameter of the side tube. However, the error attributable to this factor, even if added to errors from other causes, is so small that it is possible to obtain absolute measurements, notwithstanding the fact that the apparatus was not devised with this in view. The total error certainly does not exceed 10 per cent, and therefore it is sufficiently below the uncertainties inherent in measuring the property concerned, *viz.*, the oxidizability.

When comparative measurements are to be made, the precision attainable is greater, because the majority of the errors which affect measurements in absolute terms are compensated for. It is possible to detect extraordinarily small differences in oxidizability, even thousandths, for example, but from a practical point of view, such precision is superfluous, for only much greater differences are of any significance.

It may be said then that the precision of the apparatus is considerably greater than is necessary, and any difficulties in interpreting experimental results cannot arise from this factor.

Adjustment of the Apparatus

Attention should be directed first of all to the tightness of the system. To check this point, the proper volume of mercury is put in each chamber, the thermostat is heated to 80° C., the reaction chambers are closed, and heating is stopped. After the system has dropped to room temperature again, the mercury level should remain stationary for at least 24 hours at its particular level in each manometric tube, taking into account, of course, external thermometric and barometric changes. A few drops of a volatile liquid, *e. g.*, water or alcohol, may be put in the reaction chambers before closing them, so that part of the air is displaced by vapor. On cooling, a higher vacuum is thus obtained. However, this method is perhaps less conclusive than the first method, because the joint becomes wet and swells slightly, and this increases the tightness of the joint beyond the point attained in normal operation, and therefore runs the risk of introducing a new error.

When a leak is detected, it is corrected by changing the joints or by changing the tension on the spring which closes the particular reaction chamber. If a leak occurs during operation of the apparatus, it will be manifest by an abnormal behavior of the mercury column as it rises, or will be still more obvious by the column actually descending.

A simple and quick way of testing the tightness, proper adjustment, and satisfactory operation in general of the apparatus, all at the same time, is to carry out actual measurements of the oxidizability of the same substance in all the reaction chambers. In this case, the mercury should rise at virtually the same rate in all the manometric tubes. If this is not the case, it is necessary to ascertain whether or not differences in the mercury columns are attributable to the samples themselves. The measurements should then be repeated, either with new samples or, better still, by interchanging them.

When a very oxidizable mixture is to be tested, for instance, a vulcanizate containing neither accelerator nor antioxygen, the manometric test is carried out in only a few hours.

REPRESENTATIVE EXPERIMENTAL MEASUREMENTS

Testing of the Apparatus

To check the apparatus, it is well to choose a readily oxidizable mixture in order to shorten the time of the test and to be able to detect promptly any appreciable differences in readings which appear.

With this in mind, the following mixture was employed:

Smoked sheet	55
Sulfur	2
Diphenylguanidine	0.5
Zinc oxide	25
Carbon black	5
Talc	12.5
	100

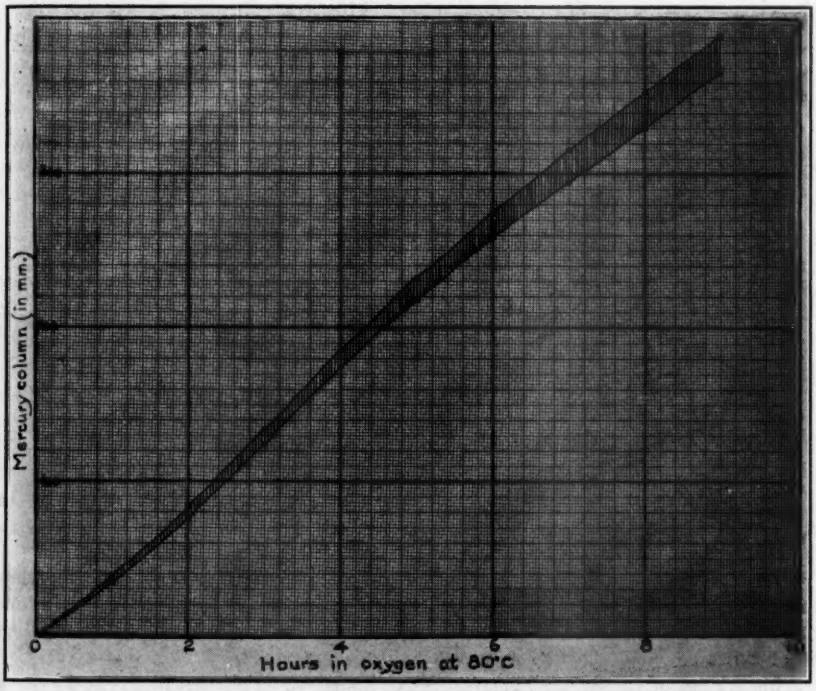

Figure 7—Checking of the Apparatus with Eleven Samples of the Same Vulcanizate
(Changes in the height of the mercury as a function of the time of heating in oxygen at 80° C. The distances between the two curves indicate the maximum variations observed between any of the eleven samples)

This mixture was milled in the ordinary way, and was vulcanized for 130 min. at 143° C.

In each tube was placed a weight of sample corresponding to 1 gram of actual rubber, *i. e.*, 1.82 grams, cut into tiny parallelopipeds approximately 2 × 3 × 3 mm. To eliminate as nearly as possible any errors arising from a lack of homogeneity of any sample, 20 grams of sample were first cut as mentioned above, and the cut-up mass was mixed thoroughly before being divided among the various tubes.

The measurements, which were carried out with the samples at 80° C., gave the results shown in Table I and Figs. 6 and 7.

The first part of the table gives the mercury levels for the various tubes after 1, 2, 3, . . . hours of heating. The second part of the same table gives the differences between two successive readings of the various individual tubes, *i. e.*, the hourly increases in height.

TABLE I

CHECKING OF THE APPARATUS

No. of Tube	Total Ascent of Mercury (in Mm.) after 1 Hr.	2 Hrs.	3 Hrs.	4 Hrs.	5 Hrs.	6 Hrs.	7 Hrs.	8 Hrs.	9 Hrs.
0	38	84	135	186	231	275	316	354	392
1	34	76	125	174	218	257	294	330	366
2	35	79	129	179	224	264	303	340	377
3	37	83	133	182	227	267	307	343	379
4	34	77	126	175	219	258	295	332	369
5	35	81	130	181	227	268	309	347	384
6	37	83	133	184	229	272	313	350	388
7	36	80	129	178	222	263	302	339	376
8	35	78	127	176	220	258	296	332	368
9	36	80	130	180	226	266	305	343	380
10	35	79	131	180	225	266	306	342	380

No. of Tube	Hourly Ascent of Mercury (in Mm.) after 1 Hr.	2 Hrs.	3 Hrs.	4 Hrs.	5 Hrs.	6 Hrs.	7 Hrs.	8 Hrs.	9 Hrs.
0	38	46	51	51	45	44	41	38	38
1	34	42	49	49	44	39	37	36	36
2	35	44	50	50	45	40	39	37	37
3	37	46	50	49	45	40	40	36	36
4	34	43	49	49	44	39	37	37	37
5	35	46	50	50	46	41	41	38	37
6	37	46	50	51	45	43	41	37	38
7	36	44	49	49	44	41	39	37	37
8	35	43	49	49	44	38	38	36	36
9	36	44	50	50	46	40	39	38	37
10	35	44	51	50	45	41	40	36	38

Figure 6 shows these results. The eleven adjoining columns represent the mercury levels in the eleven manometric tubes. The black columns indicate the hourly increases in height.

In Fig. 7, the two curves represent the rise of mercury in the two tubes in which the mercury reached the highest level and the lowest level, respectively, as a function of the number of hours of heating in oxygen. Therefore the curves of all the other tubes lie within the space between these two curves.

This spread of the curves corresponds to at least 10 per cent of the total rise of the mercury, but considering the extent to which rubber is homogeneous, this precision is all that is to be expected on the average; in fact, when results like this are obtained the apparatus may be considered to be functioning properly.

On the contrary, if, in check tests of this kind, one or more of the tubes show differences greater than those observed in these particular experiments, it should not necessarily be assumed that the apparatus is functioning improperly. Differences even as great as 20 per cent may easily be due to the heterogeneity of the rubber; in such a case this can be proved or disproved by testing more samples. On the other hand, if there is a variation greater than 20 per cent, it is most likely that there is something wrong, such as a leak in the apparatus, an error in weighing, or other source of error.

Tests with a Series of Mixtures

In the section which follows, typical data obtained by manometric measurements are given to show the influence of the percentage of sulfur on the oxidizability of a diphenylguanidine mixture.

The composition of the base mixture was the same as before:

Smoked sheet	55
Diphenylguanidine	0.5
Carbon black	5
Zinc oxide	25
Talc	12.5

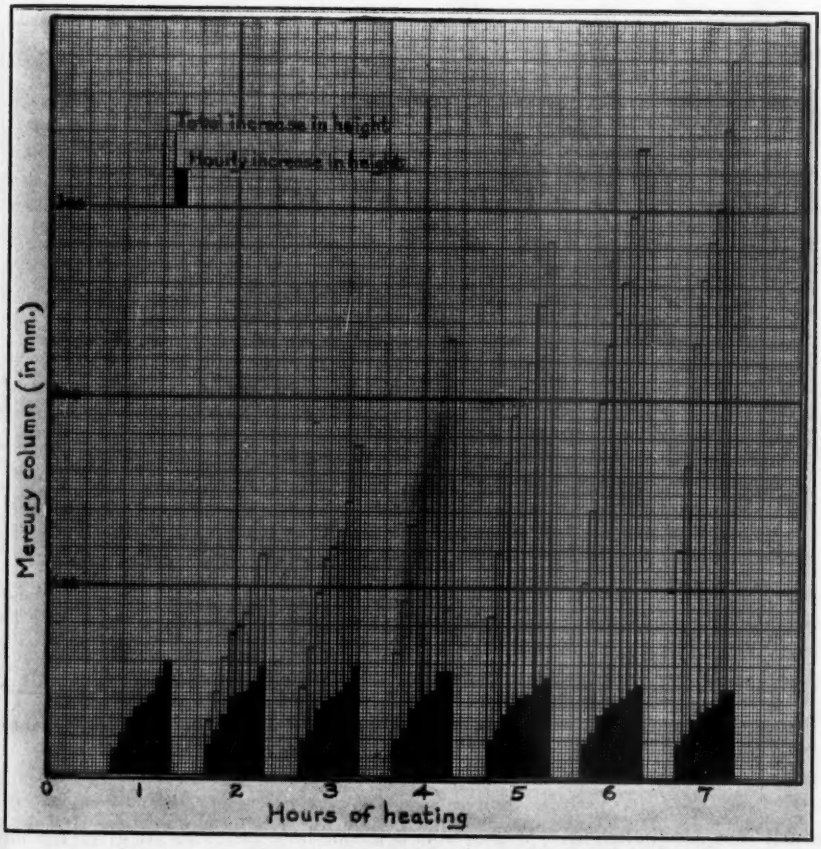

Figure 8—Influence of the Proportion of Sulfur on the Oxidizability of a Diphenylguanidine Base Mixture Containing Eight Different Percentages of Sulfur
(Total ascents and hourly ascents for times of heating from 1 to 7 hours)

To this were added from 1 to 15 parts of sulfur, and the resulting mixtures were vulcanized for 2 hours at 143° C.

The results of tests of these vulcanizates are summarized in Table II, and are also shown graphically in Figs. 8 and 9. The samples are designated by the letter S, with subscript numbers representing the number of parts of sulfur added to the

base mixture. The weight of each sample was so chosen that it contained 1 gram of actual rubber.

In these measurements, carried out as before with the samples at 80° C., one of the tubes was run empty as a control test, and at each reading the zero point of the scale was brought to the level of the mercury of the control tube to compensate for variations in atmospheric pressure and temperature. As a matter of fact these variations were practically negligible.

The graph in Fig. 8 represents the total increases in height of mercury in the eight tubes, after heating for 1, 2, 3, 4, 5, 6, and 7 hours. The black columns indicate

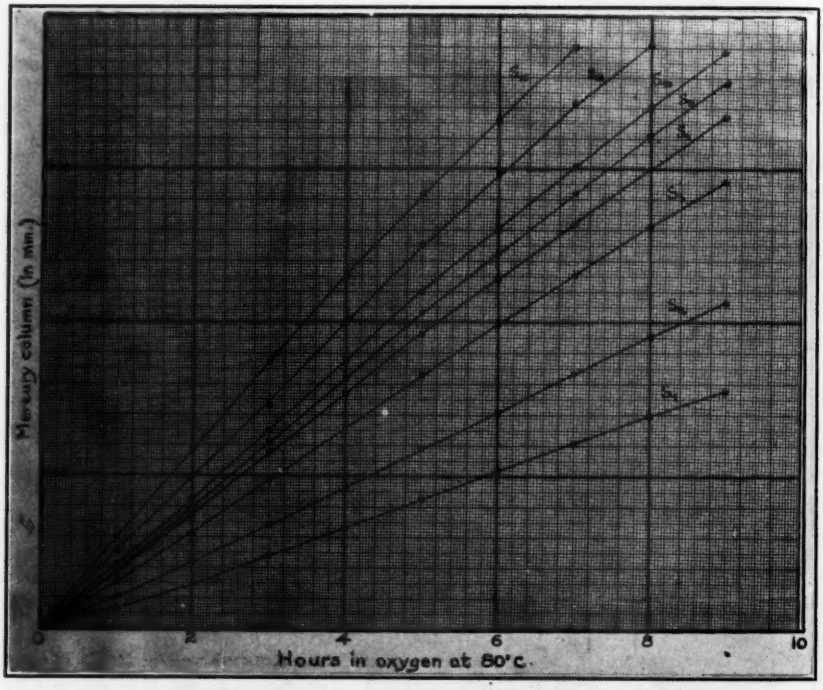

Figure 9—Influence of the Proportion of Sulfur on the Oxidizability of a Diphenylguanidine Base Mixture Containing Eight Different Percentages of Sulfur
(Changes in the height of mercury as a function of the time of heating in oxygen at 80° C.)

hourly increases in height. Measurements at one-hour intervals are given for only seven hours of heating, for after the seventh hour it was no longer possible to measure the tubes containing samples S_{15} and S_{12} because the mercury levels had reached the tops of the scales.

Finally, Fig. 9 shows the progress of oxidation of the eight samples as a function of the time of heating.

These results show very clearly the part played by sulfur, *i. e.*, the higher the percentage of sulfur, the more rapidly did the rubber mixture oxidize. Sulfur had a particularly great influence up to 4 parts; above this range the rate of oxidation became relatively less rapid with increase in the proportion of sulfur. The increase

in oxidizability with increase in sulfur from 4 to 15 parts was about the same as the increase from 1 to 4 parts.

TABLE II

INFLUENCE OF THE PERCENTAGE OF SULFUR ON THE OXIDIZABILITY OF A MIXTURE

Total Ascent of Mercury (in Mm.) after

Sample	1 Hr.	2 Hrs.	3 Hrs.	4 Hrs.	5 Hrs.	6 Hrs.	7 Hrs.	8 Hrs.	9 Hrs.
S_1	13	29	47	66	85	103	121	139	155
S_2	21	44	68	93	118	142	166	190	213
S_3	30	62	97	133	166	199	230	262	291
S_4	35	76	115	154	192	229	264	300	334
S_8	37	79	121	164	206	246	284	321	357
S_{10}	42	86	130	176	220	262	301	340	377
S_{12}	51	100	145	201	250	297	344	381	...
S_{15}	60	118	175	231	284	333	380	...	...

Hourly Ascent of Mercury (in Mm.) after

Sample	1 Hr.	2 Hrs.	3 Hrs.	4 Hrs.	5 Hrs.	6 Hrs.	7 Hrs.	8 Hrs.	9 Hrs.
S_1	13	16	18	19	19	18	18	18	16
S_2	21	23	24	25	25	24	24	24	23
S_3	30	32	35	36	33	33	31	32	29
S_4	35	41	39	39	38	37	35	36	34
S_8	37	42	42	43	42	40	38	37	36
S_{10}	42	44	44	46	44	42	39	39	37
S_{12}	51	49	45	56	49	47	47	47	..
S_{15}	60	58	57	56	53	49	47	..	..

It is obvious that after one hour of heating, the readings, though showing smaller changes in levels of the mercury, are nevertheless quite as instructive as the readings after nine hours of oxidation; in brief, the differences in level show clearly enough, even after one hour, the differences in oxidizability of the various mixtures. Particularly evident are the increases in height during the hourly intervals, as depicted in Fig. 8; in all cases these show the same order of oxidizability of the various mixtures.

These two examples make evident the precision of the manometric apparatus and the rapidity with which it will indicate the aging properties of rubber.

Acknowledgment

This apparatus has been developed in a practical way by Les Établissements Jouan of Paris, and the author wishes to express his gratitude for the coöperation of the Manager, Monsieur Jouan and the Superintendent, Monsieur Rozé.

Les Établissements Prolabo were kind enough to construct experimental apparatus, and the author expresses his thanks to Monsieur Marteret, Manager, and to Monsieur Veyrun, Technical Director.

References

[1] Charles Dufraisse, "Chemistry and Technology of Rubber," New York, **1937**, Chap. XIII, pp. 489–491.

[2] Charles Dufraisse, "La Catalyse d'Autoxydation," Traité de Grignard, Paris, **1936**, p. 1167.

[3] Another reason is the accidental presence of gases other than oxygen, resulting in differences in the composition of various parts of the system which increase with the progress of oxidation. It is equally important to reduce to a minimum this cause of errors.

[4] In general, measurements are made with a mass containing 1 gram of actual rubber to be oxidized. The volume of the sample depends on whether the mixture is more or less loaded. However, this plays little part in calculating the sensitivity, a calculation in which the aim is primarily to determine the order of magnitude.

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The Influence of Vulcanization on Oxidizability in Relation to Aging

A Preliminary Study

Charles Dufraisse and André Étienne

INSTITUT FRANÇAIS DU CAOUTCHOUC, COLLÈGE DE FRANCE, PARIS

A systematic study of the causes which contribute to the oxidation and aging of rubber has already led the present authors to investigate the part played by several factors. In an earlier publication, the action of iron was studied,[1] because it is one of the elements most likely to be present as an impurity in rubber, either by removal from the mill rolls during mixing or for various other reasons. Later[2] the effect of mastication was examined, and as a corollary, that of heating. Mastication increases slightly the oxidizability of raw rubber, but heating at 140° C. is distinctly more harmful. However, contrary to vulcanization, the influence of mastication on oxidizability and aging is hardly noticeable.

Accordingly, it is only natural for one to be prompted to study the part played by vulcanization itself, and it is, in fact, this subject with which the investigation described below is concerned.

On first examination, it is obvious that the phenomena are not at all simple. The peculiar colloidal state of the substance studied, its lack of homogeneity, a lack of methods of analysis and of research, and the difficulty of eliminating certain factors the influence of which is still in doubt, all lead to complications in such a study. Accordingly, in this preliminary work efforts were directed chiefly towards a broad study of the problem with a view to judging whether some general law might be derived to cover the various phenomena. Later the authors intend to study the various aspects of the problem in more detail.

It has been known for a long time that vulcanization, particularly overvulcanization, influences the aging properties of rubber. It was at first believed that vulcanized rubber oxidizes less rapidly than it does in the unvulcanized state.[3, 4, 5] Ahrens[4] held the view that vulcanization reduces the sensitivity to oxidation by the formation of a protective surface skin, formed by excess sulfur. It has even been affirmed that undercuring increases oxidation,[6, 7, 8] or rather that its influence varies with the nature of the ingredients present.[9] Judged by the most recent work, however, it seems that the opposite theory ought to be true. In a series of publications commencing in 1918, H. P. Stevens[10, 11] pointed out that above a certain coefficient of vulcanization, deterioration increases rapidly, *e. g.*, overcured rubber containing 9–10 per cent combined sulfur oxidizes more rapidly than rubber containing 3–4 per cent of combined sulfur.[12] The same author also emphasizes the importance of the degree of vulcanization for satisfactory natural aging.[13] Many other authors have since then confirmed these views, *i. e.*, that deterioration is accelerated by overcuring,[14, 15] and that the more pronounced is the state of undercure of rubber, the less rapid does it deteriorate. It has been proved likewise that the tendency to deteriorate is manifest in different ways according to the extent of overvulcanization; in general the rate of deterioration increases with the degree

of overvulcanization.[9, 17, 18, 19, 20, 21, 35] The temperature of vulcanization has been credited with but little influence on the aging of rubber.[22,34] This might indicate that sulfur is the agent responsible for the tendency to oxidize and to age. Now Dufraisse and Drisch,[21] and later Yamazaki and Okumura,[23] have shown that free sulfur has no influence on oxidation and aging. Consequently, the combined sulfur alone must be the deleterious agent.

Boggs and Blake[24] have offered an explanation of this phenomenon. They assume three types of rubber, soft rubber, hard rubber, and an intermediate product which is a mixture of the first two types. The hard type is the one which is chiefly responsible for oxidation. It is formed whenever the percentage of sulfur is greater than 0.5 per cent, which is the maximum percentage corresponding to the formation of soft rubber.

Moreover, it should be pointed out, as Bierer and Davis,[18] Wurm,[33] and Somerville and Russell[25] (see also de Vries and Hellendoorn[32]) have already done, that rubber mixtures containing low percentages of sulfur show particularly good aging properties. It might be mentioned in passing that the general tendency at the present time is to reduce more and more the percentage of sulfur,[25, 26] and even to eliminate it, in the latter case by restricting the sulfur to that available in certain accelerators. Then again, sulfur is now replaced, at least in part, by selenium and even by tellurium.[31]

INFLUENCE OF VULCANIZATION ON THE OXIDIZABILITY AND AGING OF INDUSTRIAL MIXTURES

Two industrial mixtures were used in the experiments. One was accelerated moderately by diphenylguanidine, the other was highly accelerated and contained an antioxygen. These two mixtures were milled in both the normal way and to excess.

MIXTURE I

Smoked sheet	55
Sulfur	2
Diphenylguanidine	0.5
Zinc oxide	25
Carbon black	5
Talc	12.5
	100

MIXTURE II

Smoked sheet	60
Sulfur	1.5
Benzothiazyl disulfide	0.15
Tetramethylthiuram disulfide	0.21
Stearic acid	1.08
Nonox-H	1.08
Zinc oxide	24
Carbon black	12
	100.02

The relative viscosities corresponded to the following rates of flow:[36]

MIXTURE I

16.6 seconds	Mixture milled normally	P
6.7 seconds	Mixture overmilled	G

MIXTURE II

2 min. 20 seconds	Mixture milled normally	T
16 seconds	Mixture overmilled	I

1. *Original Mechanical Properties and Aging.*—These mixtures were vulcanized for various times at 143° C. The aging tests were carried out in oxygen at 80° C. to the point where each sample contained 0.5 per cent of its total weight of oxygen, *i. e.*, 0.9 and 0.8 per cent, respectively, of the weight of the rubber present. To eliminate the influence of the heating itself, control samples were kept in a vacuum at the same temperature and for the same length of time as were the corresponding samples subjected to oxido-aging.

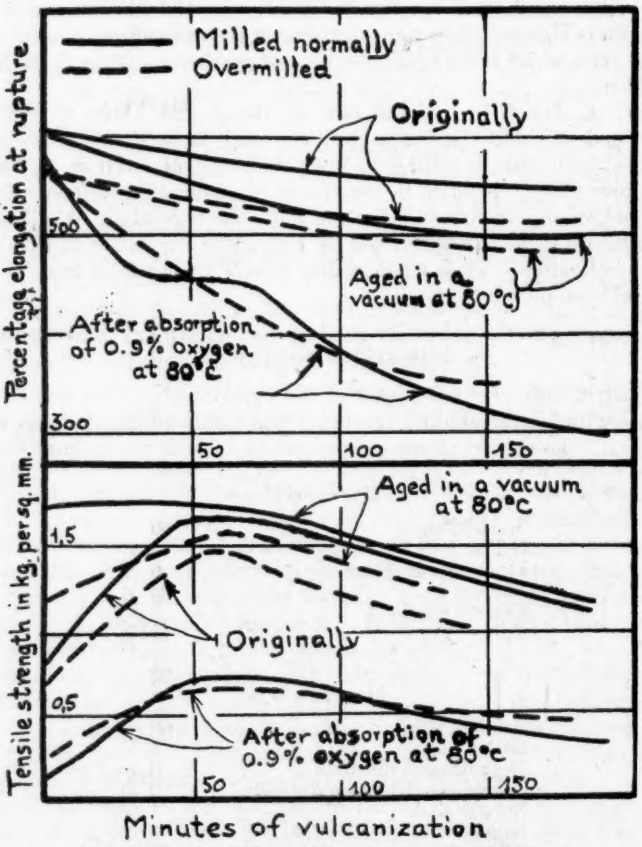

Figure 1—Aging Effects of Equal States of Oxidation

The mechanical properties as a function of the time of vulcanization at 143° C. of two series of samples accelerated by diphenylguanidine (one series milled normally, the other series milled excessively), before and after aging at 80° C. in a vacuum and in oxygen. In all cases the oxidized samples absorbed 0.9 per cent oxygen, based on the rubber. The corresponding oxidizability data are shown in Figs. 3 and 4

The mechanical tests of the samples in their original form and after aging are shown in Figs. 1, 1a, and 2, where the mechanical properties are shown as a function of the time of vulcanization.

2. *Oxidizability.*—The results of oxidizability tests on another set of samples like those which were aged in oxygen are shown in Figs. 3, 4, 5, and 6. Although

the oxidizability had already been studied by a series of measurements of the oxido-aging of the samples described above, it was considered advisable to repeat the tests with another series, because in the first series rings cut for mechanical testing were used, and their dimensions were relatively great. These large dimensions would have necessitated large chambers and large volumes of gas, with resulting sacrifice of precision. The new series of measurements were carried out in each

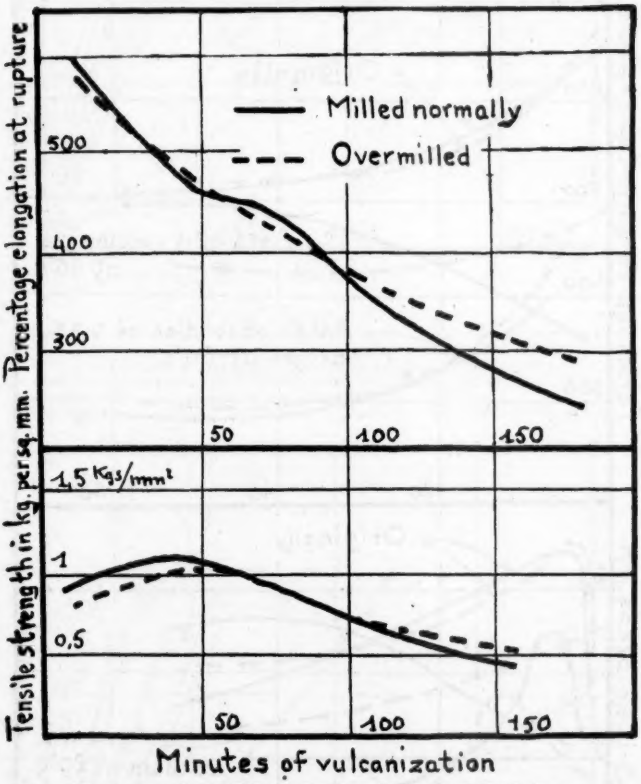

Figure 1a—Aging Effects for Equal Times of Oxidation

The mechanical properties as a function of the time of vulcanization at 143°. C. of two series of samples accelerated by diphenylguanidine (one series milled normally, the other series milled excessively), after aging for 10 hours in oxygen at 80° C. The curves were constructed by interpolation by combining data in Figs. 1, 3, and 4 and assuming that the degree of oxidation and the corresponding changes in mechanical properties are proportional. This method of representation gives curves similar to ordinary aging curves

case with only one gram of each sample in 8 cc. of oxygen; the technic was the usual one. The results of the measurements are summarized in Figs. 7, 7a, 8, 9, and 9a, and will be of particular help in comparing results obtained later.

(*a*) *Mixtures accelerated by diphenylguanidine* (Figs. 1, 1a, 3, 4, 7, and 7a).—Initially the optimum point of vulcanization was the same, regardless of the degree to which a mixture was masticated; the tensile strength of the overmilled sample was slightly less than that of the corresponding normally milled sample, but this small difference tended to disappear after aging.

The effect of heating at 80° C. in a vacuum (Fig. 1) did not seem to have any influence on the overcured samples, but it did bring about an after-vulcanization (with improvement in the mechanical properties) of the undercured samples, so

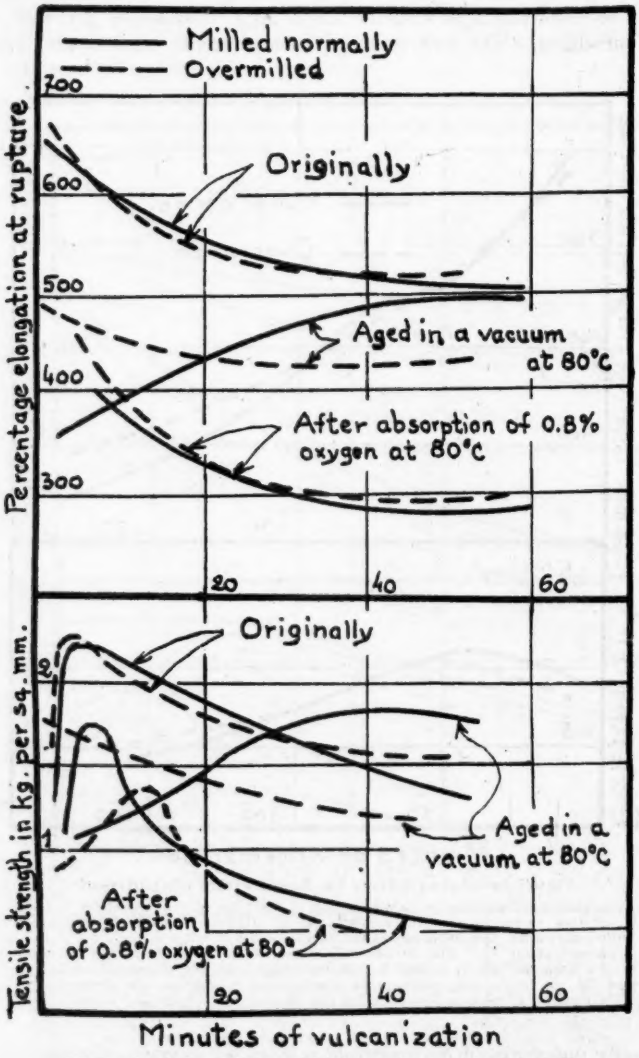

Figure 2—Aging Effects at Different States of Oxidation

The mechanical properties as a function of the time of vulcanization at 143° C. of two series of samples accelerated by tetramethylthiuram disulfide (one series milled normally, the other series milled excessively) before and after aging at 80° C. in a vacuum and in oxygen

In all cases, the oxidized samples absorbed 0.8 per cent of oxygen, based on the rubber. The corresponding oxidizability data are shown in Figs. 5 and 6

that for a given proportion of oxygen absorbed, the lowering of mechanical properties due to oxidation, based on the samples heated at 80° C. in a vacuum, was

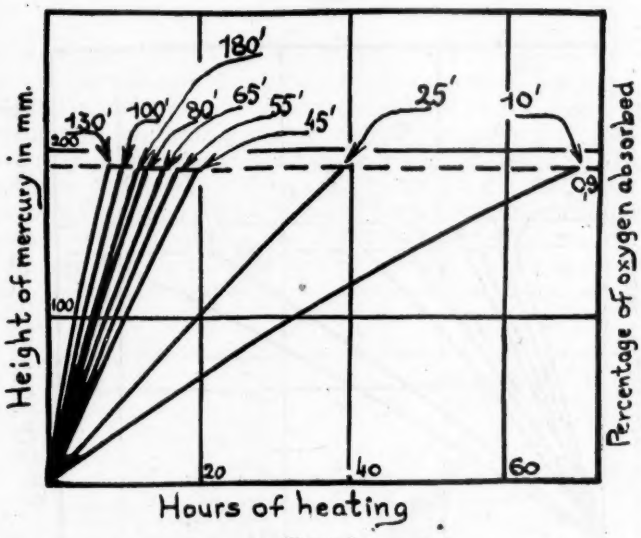

Figure 3

Influence of the time of vulcanization at 143° C. on the oxidizability at 80° C. of a mixture accelerated by diphenylguanidine, milled normally, and cut into ring test-specimens ready for mechanical testing
In every case, oxidation was stopped when 0.9 per cent of oxygen, based on on the rubber had been absorbed
The figures pointing to the curves indicate the times of vulcanization

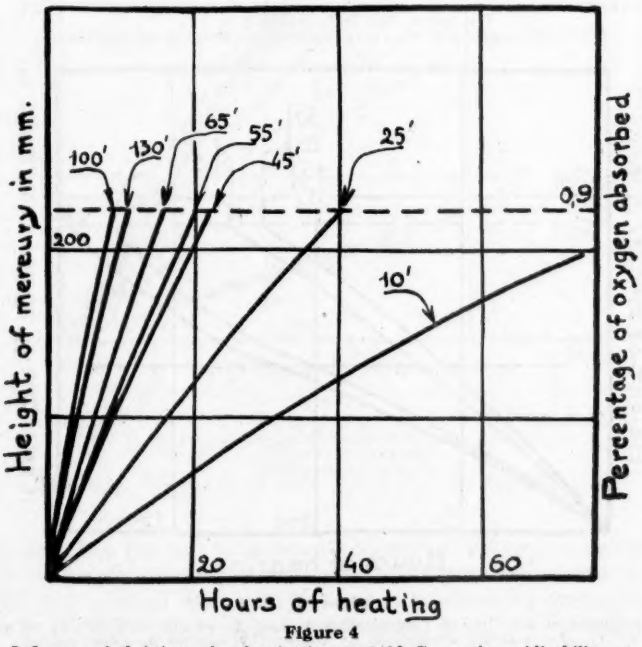

Figure 4

Influence of the time of vulcanization at 143° C. on the oxidizability at 80° C. of a mixture accelerated by diphenylguanidine, milled excessively, and cut into ring test-specimens ready for mechanical testing
In every case, oxidation was stopped when 0.9 per cent of oxygen, based on the rubber, had been absorbed
The figures pointing to the curves indicate the times of vulcanization

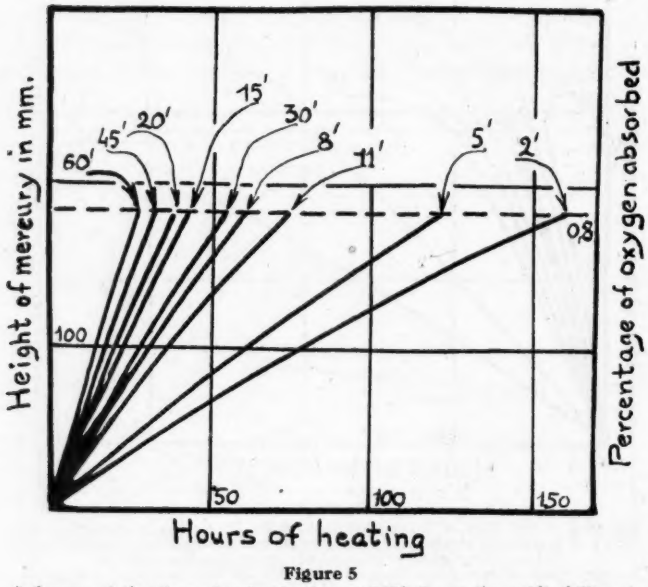

Figure 5

Influence of the time of vulcanization at 143° C. on the oxidizability at 80° C. of a mixture accelerated by tetramethylthiuram disulfide, mixed normally, and cut into test-specimens ready for mechanical testing
In every case oxidation was stopped when 0.8 per cent of oxygen, based on the rubber, had been absorbed
The figures pointing to the curves indicate the times of vulcanization

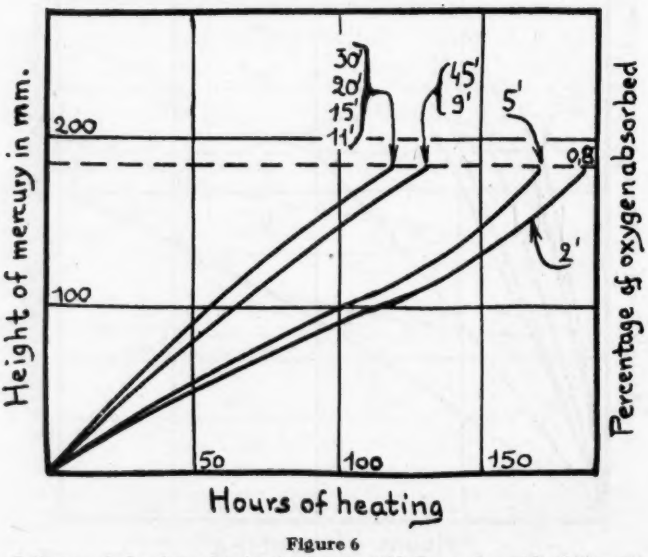

Figure 6

Influence of the time of vulcanization at 143° C. on the oxidizability at 80° C. of a mixture accelerated by tetramethylthiuram disulfide, milled excessively, and cut into ring test-specimens ready for mechanical testing
In every case oxidation was stopped when 0.8 per cent of oxygen, based on the rubber, had been absorbed
The figures pointing to the curves indicate the times of vulcanization

relatively more pronounced in the case of undercured samples than in the case of overcured samples. Then again a tendency to become sticky and soft, in a manner resembling the behavior of raw rubber, was evident in the undercured samples (10 and 25 min.). Accordingly, oxygen seems to bring about aging more rapidly than heat brings about after-vulcanization, or else this latter effect is inhibited by the oxidation.

The results in Figs. 3 and 4 show, in accord with facts already known, that undercured samples are less rapidly oxidized than are overcured samples, *i. e.*, overcured samples age more rapidly than undercured samples. It is always preferable to undercure in the neighborhood of the optimum point rather than to overcure.

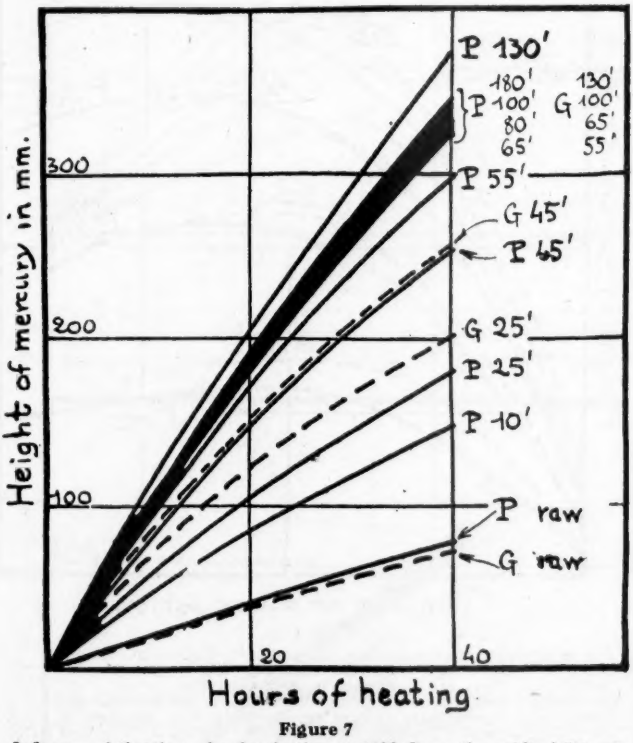

Figure 7
Influence of the time of vulcanization at 143° C. on the oxidizability at 80° C. of two mixtures accelerated by diphenylguanidine
P mixture milled normally
G mixture milled excessively
The figures pointing to the curves indicate the times of vulcanization

Nevertheless, it is not true that the rate of oxidation increased indefinitely with increase in the time of vulcanization; it seemed rather to approach a plateau effect (see Figs. 3 and 4, and 7 and 7a). Consequently, excessive overcuring is not so dangerous as might be supposed, at least from the point of view of a tendency to oxidize. Its effect is chiefly to lower the original mechanical properties before any deterioration has taken place, and although this inferiority persists throughout aging, it does not become disproportionately greater.

NOTE. If, as a first approximation, a proportionality between the changes in mechanical properties and the progress of oxidation is assumed, it is possible to calculate by interpolation the changes in mechanical properties of diphenylguanidine mixtures as a function of the time of aging. Curves are thus obtained (see Fig. 1a) which are analogous to those obtained in industrial work with the Geer oven and the Bierer-Davis oxygen bomb. This is evidence of the fact that the manometric method is not lacking in interest from a practical point of view.

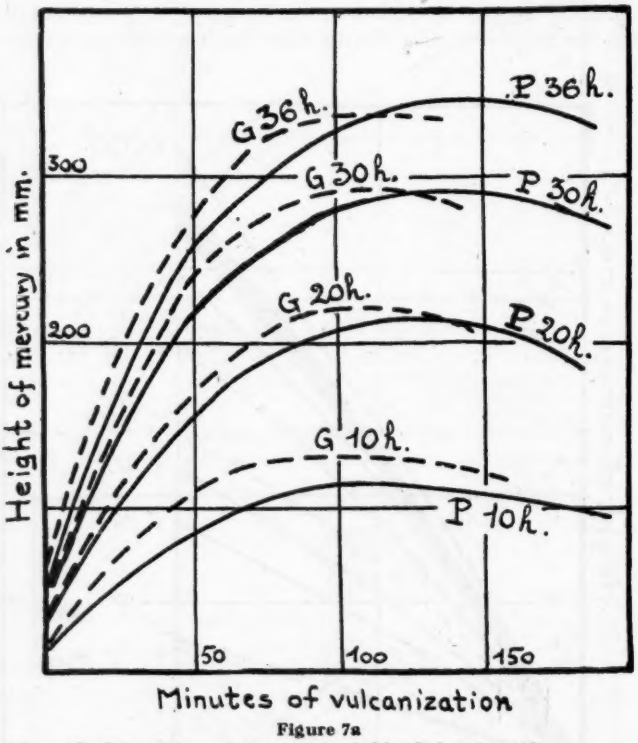

Figure 7a

The oxidizability of two mixtures accelerated by diphenylguanidine:
P mixture milled normally
G mixture milled excessively
after heating at 80° C. as a function of the time of vulcanization at 143° C. These curves reproduce in another system of variables the data in Fig. 7, and show the results of 10, 20, 30 to 36 hours' heating in oxygen at 80° C. The figures accompanying each curve indicate the number of hours of heating at 80° C. in oxygen

(*b*) *Mixtures accelerated by tetramethylthiuram disulfide* (Figs. 2, 5 and 6, 8, 9, and 9a).—With the mixture accelerated by tetramethylthiuram disulfide, the results were less well defined than with that containing diphenylguanidine. As seen in Fig. 2, the curve representing the change in tensile strength as a function of the time of vulcanization shows a very sharp maximum, the position of which seems to be independent of the extent of mastication. On the other hand, after oxidation has occurred, this optimum for the overmilled sample is displaced at the right. In the case of the normally milled sample this displacement is inappreciable. Furthermore, after oxidation the tensile strength, relative to this optimum, is lower

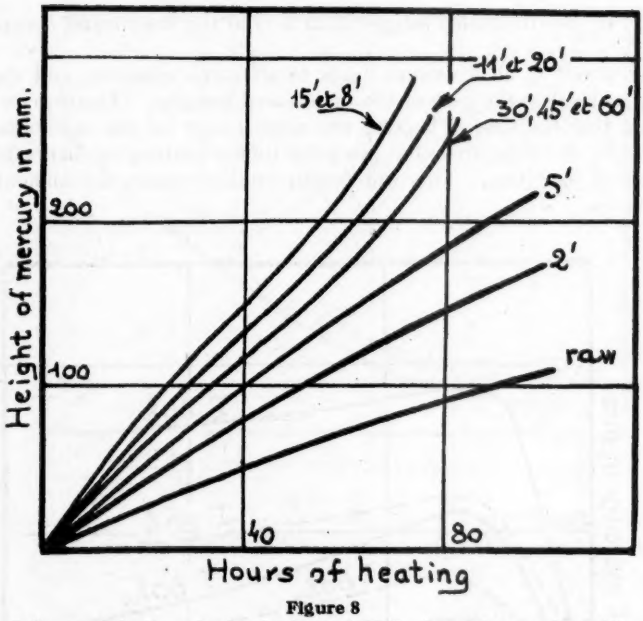

Figure 8

Influence of the time of vulcanization at 143° C. of a mixture accelerated by tetramethylthiuram disulfide, and milled normally, on its oxidizability at 80° C.

The figures accompanying the curves indicate the times of vulcanization

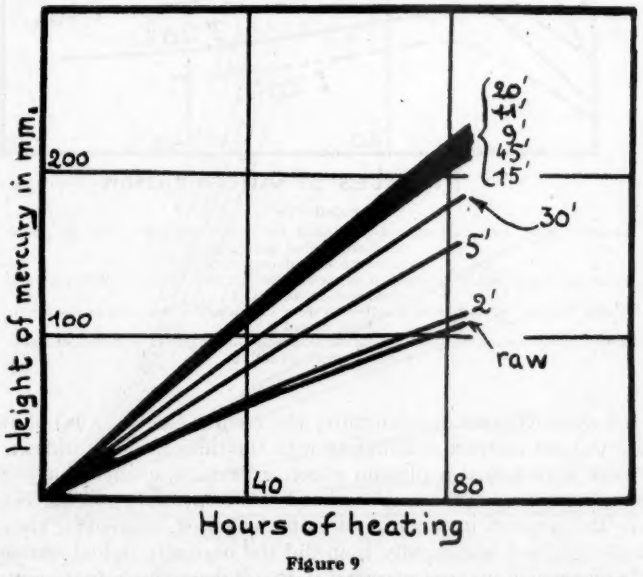

Figure 9

Influence of the time of vulcanization at 143° C. of a mixture accelerated with tetramethylthiuram disulfide, and milled excessively, on its oxidizability at 80° C.

The figures accompanying the curves indicate the times of vulcanization

in the case of the overmilled sample than it is in the case of the normally milled sample.

Heating at 80° C. in a vacuum leads to after-vulcanization, and this effect is especially marked in the case of the undercured samples. This can be explained by the fact that the time of heating was much longer for the undercured samples than it was for the overcured ones, since this time of heating was an inverse function of the rate of oxidation. This will doubtless also explain the anomalies shown by the curves.

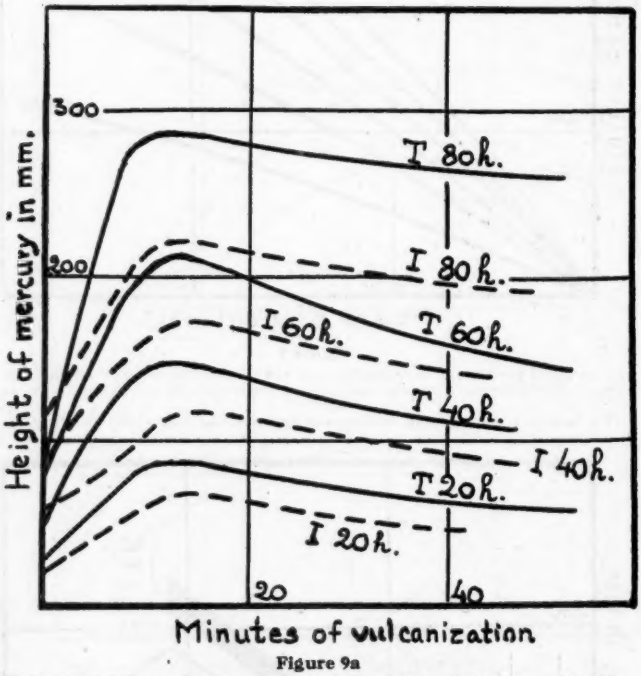

Figure 9a

Oxidation of two mixtures accelerated by tetramethylthiuram disulfide:
T mixture milled normally
I mixture milled excessively
after various times of heating in oxygen at 80° C. as a function of the time of vulcanization at 143° C.
These curves reproduce in another system of variables the results shown in Figs. 8 and 9
The figures accompanying the curves indicate the numbers of hours of heating in oxygen at 80° C.

As for the diphenylguanidine mixture, the results (see Fig. 9a) show that the oxidizability did not increase indefinitely with the time of vulcanization, but seems rather to have approached a plateau effect or perhaps even to have diminished. This plateau commences in the neighborhood of the optimum point of vulcanization (10 min. in the present instance). It is to be noted, moreover, that the overmilled sample oxidized less rapidly than did the normally milled sample, a difference in behavior which was not manifest in the diphenylguanidine mixture.

Let it be emphasized once more in passing that in this sort of measurements fluctuations occur, particularly with ultra-accelerated mixtures. With the latter

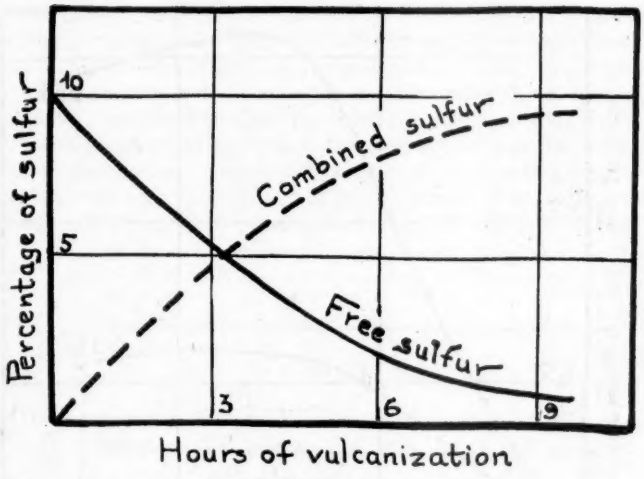

Figure 10

Percentages of free sulfur and of combined sulfur in an industrial mixture accelerated with diphenylguanidine, milled normally (mixture P) as functions of the time of vulcanization at 143° C.

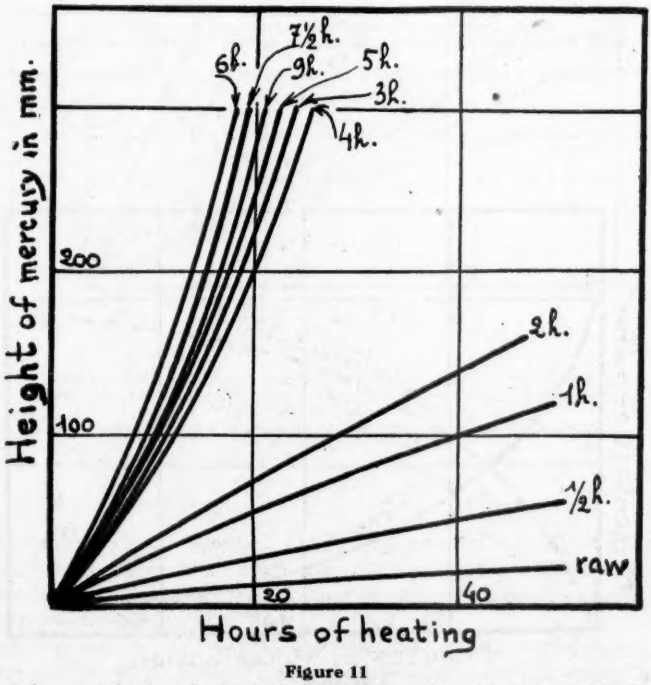

Figure 11

Influence of the time of vulcanization at 143° C. on the oxidizability at 80° C. of a simple mixture (smoked sheet 100, sulfur 10)
The figures accompanying the curves indicate the times of vulcanization

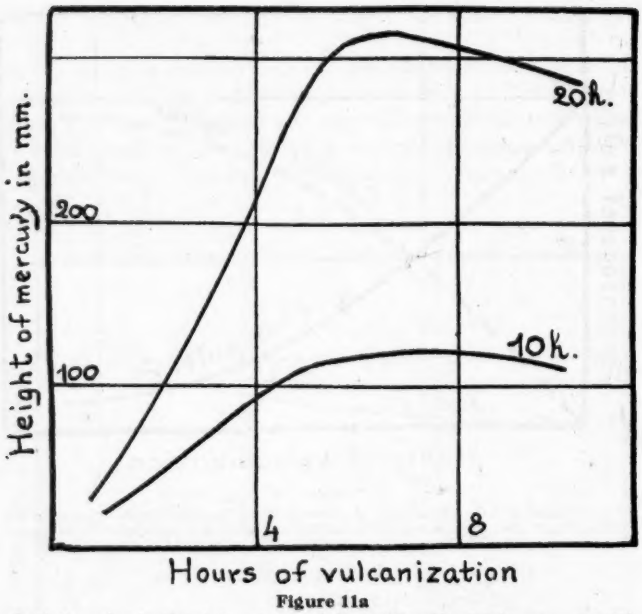

Figure 11a

Oxidation of a simple mixture (smoked sheet 100, sulfur 10) in oxygen at 80° C. as a function of the time of vulcanization at 143° C.
These curves reproduce in another system of variables the results shown in Fig. 11
The figures on the curves indicate the number of hours of heating in oxygen at 80° C.

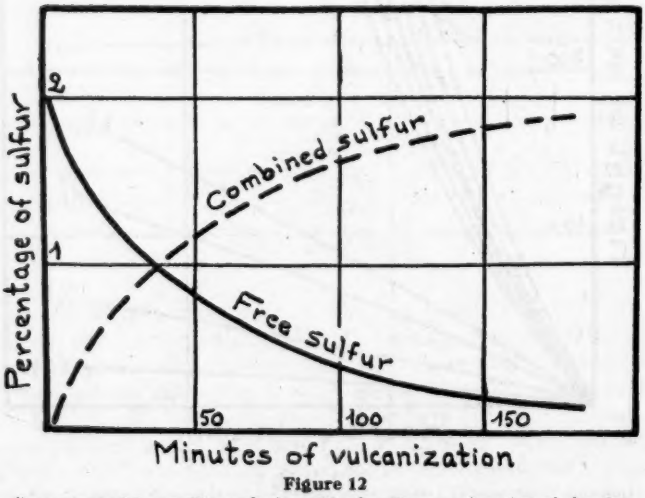

Figure 12

Percentage of free sulfur and of combined sulfur as a function of the time of vulcanization at 143° C. of a simple mixture of smoked sheet 100, sulfur 10

still more than with other types of mixtures, the intensity of the reactions which take place during vulcanization lead inevitably to certain irregularities. It should be added at once, however, that these irregularities are far from great enough to modify in any way the conclusions, because the latter have been drawn with a margin of safety sufficient to allow for these irregularities. In view of this, the conclusion seems warranted that both in the case of mixtures accelerated by tetramethylthiuram disulfide and those accelerated by diphenylguanidine vulcanization did not increase the oxidizability indefinitely. A high degree of overcuring has then an abnormally harmful effect only on the original mechanical properties and

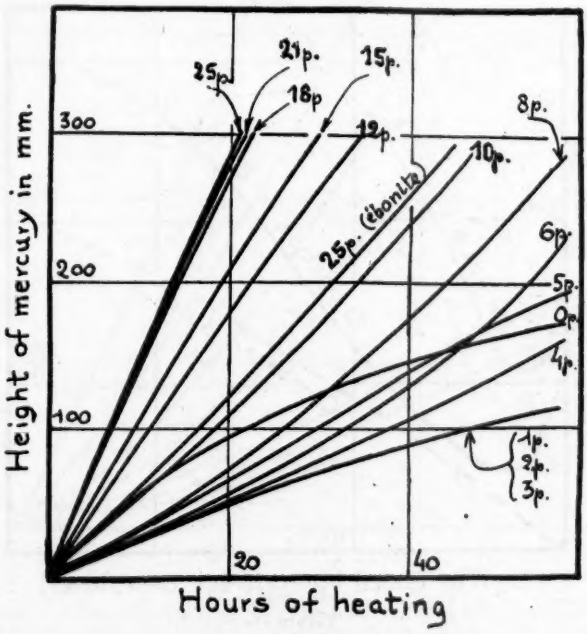

Figure 13

Influence of the proportion of sulfur on the oxidizability at 80° C. of mixtures composed of smoked sheet 100, diphenylguanidine 1, sulfur 0 to 25, vulcanized for 2 hours at 143° C.
The figures accompanying the curves indicate the proportions of total sulfur in the mixtures

not on the oxidizability. Overcuring leaves the product initially in a state of mechanical inferiority, hence with apparently poorer aging properties than after having been vulcanized to the optimum point; this difference is, however, only attributable in part to a greater oxidizability.

It should, moreover, be pointed out that the mixture accelerated by tetramethylthiuram disulfide showed fairly good resistance to oxidation, as the mechanical properties and aging properties of mixtures of this kind would lead one to suppose.

1. Oxidizability of the Industrial Diphenylguanidine Mixture Already Tested

The curves of oxidizability as a function of the time of vulcanization for different times of heating at 80° C. (see Fig. 7a) have almost the same trend as the classic curves representing the percentage of combined sulfur as a function of the time of vulcanization. From this it might be supposed that the active agent responsible for the oxidizability of the vulcanizate is sulfur in its combined forms. This impression is supported by the results of determinations which were carried out on the diphenylguanidine mixture[37] (see Fig. 10); the curve of combined sulfur does not

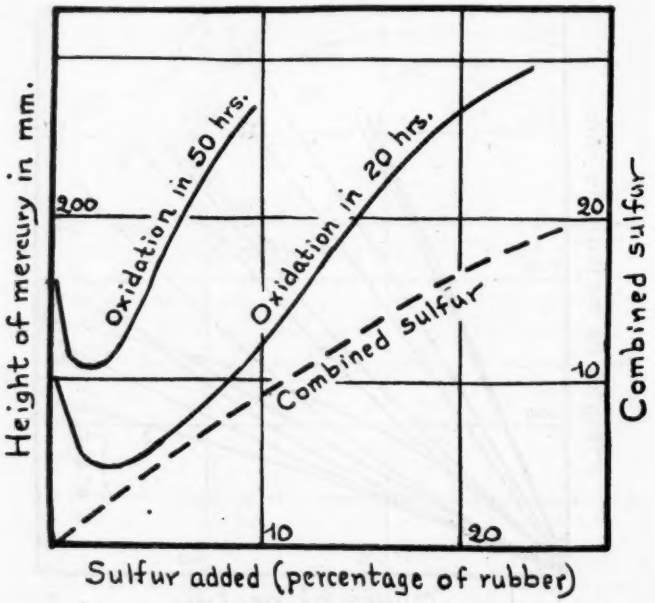

Figure 13a

Oxidation in oxygen at 80° C. of mixtures composed of smoked sheet 100, diphenylguanidine 1, and sulfur in various proportions, and vulcanized for 2 hours at 143° C., as a function of the proportion of sulfur
These curves reproduce in another system of variables the results shown in Fig 13.
A curve of the changes in combined sulfur as a function of the total sulfur added is also included (the ordinate scale in this case is on the right)

differ essentially from the curve of oxidizability as a function of the time of vulcanization (Fig. 7a).

2. Oxidizability of a Simple Rubber-Sulfur Mixture Vulcanized for Different Lengths of Time, without Accelerator

In an effort to confirm the influence of combined sulfur on oxidizability, a mixture containing a relatively high percentage of sulfur (10 parts per 100 parts of smoked sheet) without any accelerator was vulcanized at 143° C. from 30 min. to 9 hours. The oxidizability of the resulting vulcanizates is shown in Figs. 11 and 11a.

It is evident from Fig. 11a that, as before, the oxidizability became stabilized beyond a certain time of vulcanization. There was, in fact, a slight diminution in the oxidizability, but only for mixtures vulcanized for long periods so that they became hard and therefore little permeable to gases.

The oxidizability was then compared with the percentages of free sulfur and combined sulfur.[38] The results, given in Fig. 12, show a law of change analogous to that already found, *i. e.*, the oxidizability of the vulcanizates seems here also to have depended on the sulfur combined with the rubber.

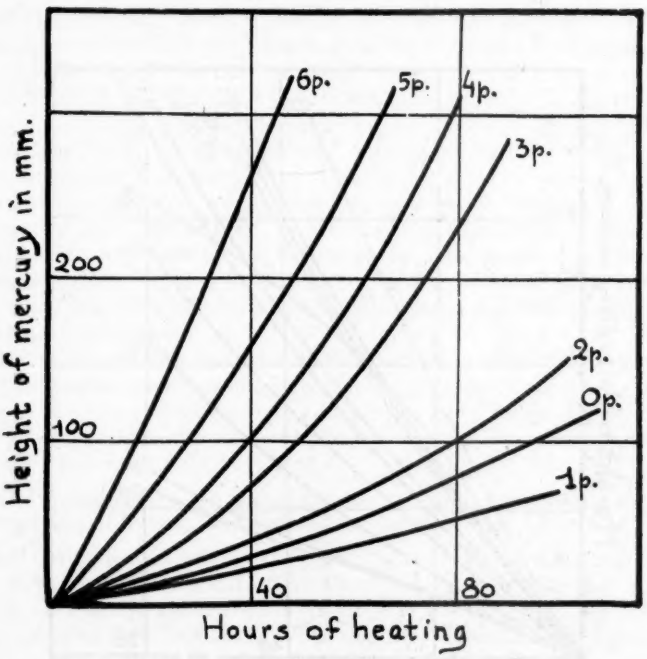

Figure 14
Influence of the proportion of sulfur on the oxidizability at 80° C. of simple mixtures (crepe 100, sulfur 0 to 6) vulcanized for 5 hours at 143° C. The values accompanying the curves indicate the proportion of total sulfur in the mixtures

3. Oxidizability of Simple Mixtures Containing Various Proportions of Sulfur, and Vulcanized for the Same Length of Time

After having employed constant proportions of sulfur and different times of vulcanization, it was considered of interest to study the effect of keeping the time of vulcanization constant but varying the percentage of sulfur. Mixtures of smoked sheet 100, diphenylguanidine 1, and sulfur 0 to 25 were tested. The time of milling as well as the time of vulcanization, which was 2 hours at 143° C., was the same for all the samples, including the control sample. With 25 parts of sulfur, the product was hard, but a true ebonite was not obtained except by an additional 2 hours of vulcanization. The majority of the mixtures were considerably overcured, as a matter of fact intentionally, in order to obtain a high percentage of combined sulfur.

In the first place, the oxidizability of each vulcanizate was measured with samples containing in each case 1 gram of actual rubber (see Figs. 13 and 13a). In the second place, the percentages of combined sulfur were determined. The results are shown in Fig. 13a, in which the combined sulfur is shown as a function of the total sulfur present. This is practically a linear function.

Here oxidizability was not a simple linear function of the combined sulfur, in fact it seemed to give indications of a minimum. In particular the control mixture without sulfur, after simply heating like the other mixtures, for 2 hours at 143° C., oxidized more rapidly at the beginning (see Fig. 13) than did the mixtures containing small percentages of sulfur, *i. e.*, oxidation started at a faster rate. How-

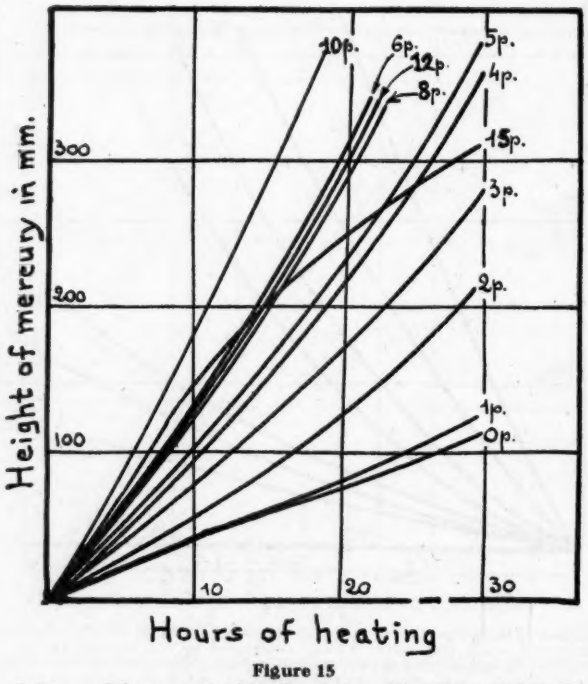

Figure 15

Influence of the proportion of sulfur on the oxidizability at 80° C. of loaded mixtures (smoked sheet 55, diphenylguanidine 0.5, zinc oxide 25, carbon black 5, talc 12.5, sulfur 0 to 15) vulcanized for 2 hours at 143° C.

The figures accompanying the curves indicate the proportions of total sulfur in the mixtures

ever, after a certain time of oxidation, the rate tended towards a fixed normal value. Consequently, the minimum becomes less noticeable with increase in the extent of oxidation.

This curious observation is in accord with the views of Boggs and Blake regarding the extremely marked oxidizability of the intermediate sulfurated member of the rubber-sulfur series. However, the action of heat alone on raw rubber must not be overlooked for, as has already been shown in an earlier publication,[2] this is an important influence, and it is sufficient in itself to explain the phenomenon, as will be seen later.

Since there is no direct relation between oxidizability and combined sulfur, there are other agencies at work. As already shown,[21] this cannot be explained by free sulfur, and the fact has been verified once more with various unvulcanized samples employed in the preparation of the vulcanizates described above.

With a view to explaining the rather abnormal phenomenon of a minimum point in the oxidizability, a series of tests were made with crepe rubber containing 0 to 6 parts of sulfur, but no accelerator or filler. All the mixtures were vulcanized for the same length of time, *viz.*, 5 hours, at 143° C., a time of heating chosen as sufficiently long to give a relatively high proportion of combined sulfur. Each mixture was also milled for the same length of time, so that the influence of this factor would be eliminated. In measuring the oxidizability of the vulcanized products, samples corresponding in weight to 1 gram of actual rubber were used in each case (see Fig. 14). Again it was found that the oxidizability increased with increase in the quantity of sulfur added, and therefore in turn with the quantity of combined sulfur. Furthermore, as in the case of the preceding mixture containing smoked sheet and diphenylguanidine, the sample heated without sulfur for 5 hours at 143° C. oxidized more rapidly than the sample vulcanized with 1 per cent of sulfur. The minimum already described would therefore seem to be confirmed; and consequently, heating would be an agent in itself tending to increase oxidizability, and this latter would be reduced by the very first combined sulfur which is produced. With increase in the proportion of combined sulfur, the antagonism between the two reactions would gradually become insignificant in the face of the accelerating action of the combined sulfur itself.

The oxidizability of these vulcanizates without any accelerator was greater than that of mixtures containing the same percentage of sulfur and also diphenylguanidine. Accordingly, the effect of diphenylguanidine must be to reduce the oxidizability, doubtless by diminishing the time of vulcanization, for its antioxygenic power is only slight.[21]

4. The Oxidizability of Loaded Rubber Mixtures Containing Various Percentages of Sulfur, and Vulcanized for the Same Length of Time

It seemed desirable next to vary the percentage of sulfur in a mixture containing inorganic fillers or pigments and an accelerator (diphenylguanidine) in the same proportions as in the samples which were employed to study the influence of vulcanization on aging (see Section 1). The mixture chosen had the following composition:

Smoked sheet	55
Diphenylguanidine	0.5
Zinc oxide	25
Carbon black	5
Talc	12.5
Sulfur	1 to 15 per cent, based on the rubber

All the mixtures were milled in an identical manner, and all were then vulcanized for 2 hours at 143° C.

The oxidizability of the mixtures before and after vulcanization was measured with samples of weights corresponding in all cases to 1 gram of rubber. As in the previous experiments, the unvulcanized samples showed nearly the same oxidizability. This again shows that free sulfur has no influence on the rate of oxidation of rubber.

The results obtained with the samples after vulcanization are shown in Figs. 15 and 15a. The percentages of free sulfur in the various mixtures were first determined, and the combined sulfur values calculated by difference. Figure 15a shows

the changes in oxidizability as a function of the percentage of total sulfur, and also as a function of the percentage of combined sulfur.

The oxidizability seems to pass through a well-defined maximum at a point corresponding to 10 parts of total sulfur, although the maximum for the mixture containing no filler has more of the form of a plateau. On the contrary, the minimum shown by this unloaded mixture with low percentages of sulfur seems to disappear completely. The fillers certainly play a part in these differences, in fact it is already known that carbon black has a pronounced effect on oxidizability.

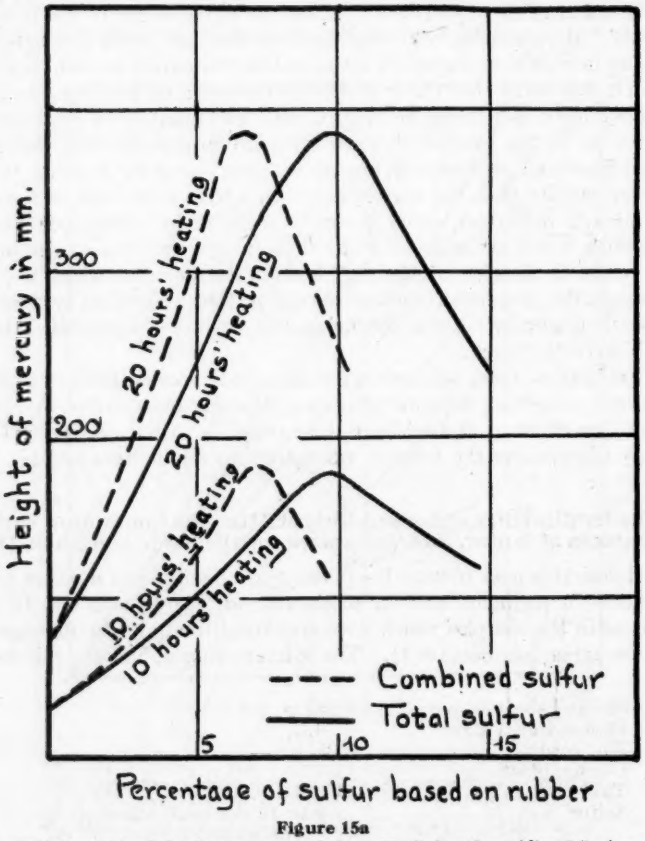

Figure 15a

Oxidation of loaded mixtures (smoked sheet 55, diphenylguanidine 0.5, zinc oxide 25, carbon black 5, talc 12.5, sulfur various proportions), vulcanized for 2 hours at 143° C. in oxygen at 80° C. as a function both of the proportion of total sulfur added and of the quantity of combined sulfur
These curves reproduce in another system of variables the results shown in Fig. 15

5. The Influence of the Proportion of Sulfur on the Oxidizability of Simple Mixtures Accelerated Either with Tetramethylthiuram Disulfide or with Tetramethylthiuram Monosulfide

These mixtures were prepared with percentages of sulfur varying from 0 to 4 per cent, based on the rubber. This range includes the proportions of sulfur actually used in practice. The mixtures had the following compositions:

Smoked sheet	100
Sulfur	0 to 4
Tetramethylthiuram disulfide or monosulfide	0.5
Zinc oxide	5

All mixtures were milled for the same length of time, and in all cases were vulcanized for 10 min. at 120° C.

The oxidizability of the various mixtures at 80° C., both before and after vulcanization, was measured with samples containing in every case 1 gram of rubber. The results are shown in Figs. 16 and 17.

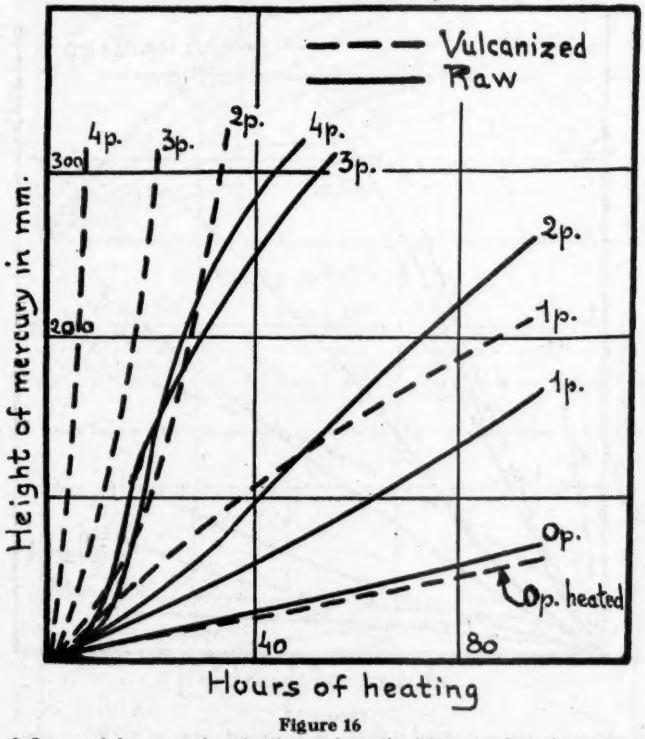

Figure 16

Influence of the proportion of sulfur on the oxidizability at 80° C. of mixtures of smoked sheet 100, tetramethylthiuram disulfide 0.5, zinc oxide 5, sulfur 0 to 4, before and after vulcanizing for 10 min. at 120° C.
The figures accompanying the curves indicate the proportions of total sulfur in the mixtures

In the case of the unvulcanized mixtures, the oxidizability was a function of the quantity of sulfur present. This might seem to be contradictory to the results published earlier, according to which free sulfur had almost no influence on oxidizability. Actually however, there is no such contradiction, for with such active accelerators present, heating at 80° C. brought about considerable vulcanization, as was quite evident at the end of the test. It should also be noted that the oxidizability curves of the unvulcanized samples (see Figs. 16 and 17) show points of inflection and a rapid acceleration of the oxidizability in proportion to the sulfur

which combined. It is then in the combined state, not in the free state, that sulfur accelerates oxidation.

In the same way it is possible to explain why, in the presence of tetramethylthiuram disulfide, no minimum point in the oxidizability appears with increase in the sulfur content above the 0 point, as occurred in the cases already described. In its capacity as a sulfide, this accelerator doubtless has the power of vulcanizing rubber at the expense of its sulfur of constitution. This explains why mixtures containing

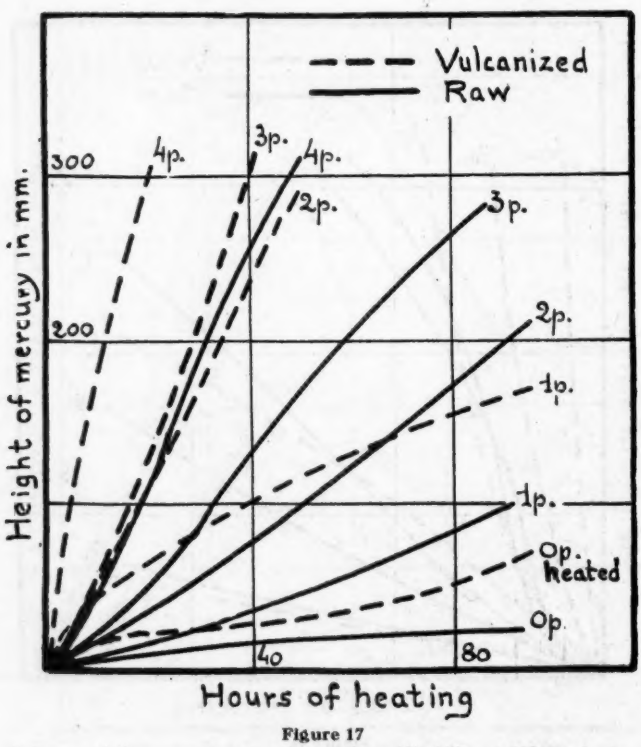

Figure 17

Influence of the proportion of sulfur on the oxidizability at 80° C. of mixtures of smoked sheet 100, tetramethylthiuram monosulfide 0.5, zinc oxide 5, sulfur 0 to 4, before and after vulcanizing for 10 min. at 120° C. The figures accompanying the curves indicate the proportions of total sulfur in the mixtures

no additional sulfur, but containing tetramethylthiuram disulfide, vulcanized slightly, enough, in fact, to reach or even to exceed the degree of vulcanization to which the minimum oxidizability corresponded. Although tetramethylthiuram monosulfide is considered to be incapable of bringing about vulcanization without additional sulfur, the same explanation may hold true for this accelerator, for the degree of vulcanization which supposedly took place was in the present case only very slight.

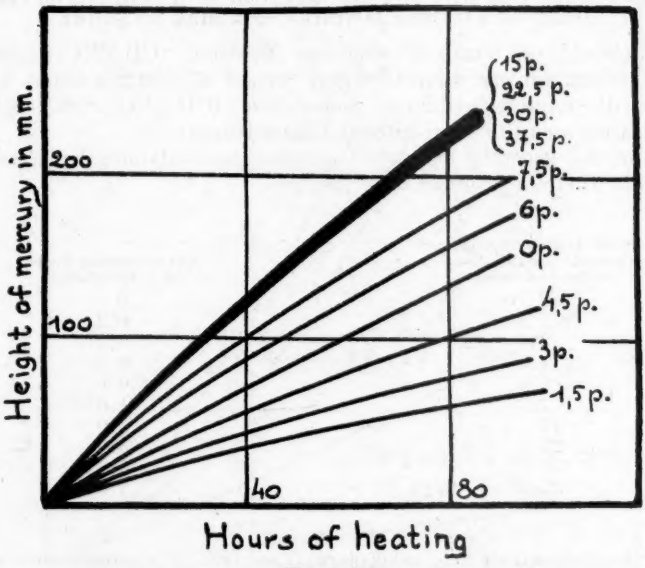

Figure 18

Influence of the proportion of tetramethylthiuram disulfide on the oxidizability at 80° C. of mixtures of smoked sheet 100, zinc oxide 5, tetramethylthiuram disulfide 0 to 37.5, vulcanized for 10 min. at 120° C.
The figures accompanying the curves indicate the proportion of tetramethylthiuram disulfide in the mixtures

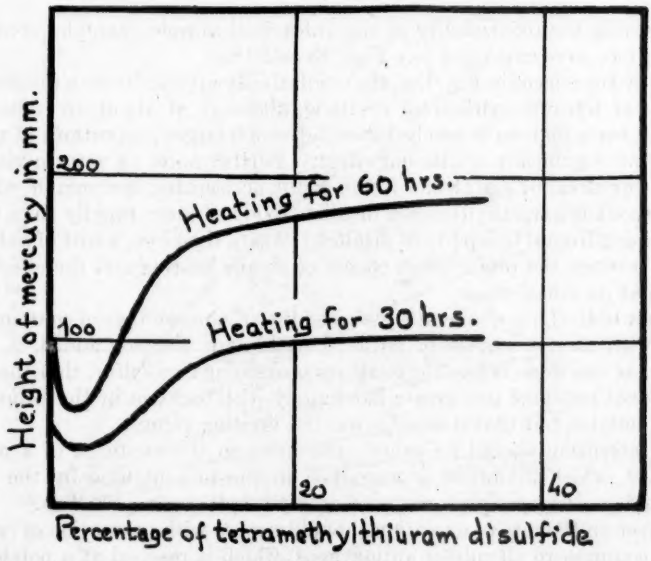

Figure 18a

Oxidation of mixtures of smoked sheet 100, zinc oxide 5, tetramethylthiuram disulfide various proportions, vulcanized for 10 min. at 120° C. in oxygen at 80° C. as a function of the proportion of tetramethylthiuram disulfide
These curves reproduce in another system of variables the results shown in Fig. 18

6. Influence of the Quantity of Tetramethylthiuram Disulfide on the Oxidizability of a Rubber Mixture Containing No Sulfur

Each molecule of tetramethylthiuram disulfide, $(CH_3)_2NC(:S)SSC(:S)N(CH_3)_2$, must contain one atom of sulfur capable of bringing about vulcanization, for with tetramethylthiuram monosulfide, $(CH_3)_2NC(:S)SC(:S)N(CH_3)_2$, no vulcanization seems to occur without auxiliary sulfur.

In view of this generally accepted fact, mixtures containing large percentages of tetramethylthiuram disulfide were prepared.

Parts of Tetramethylthiuram Disulfide per 100 Parts of Smoked Sheet	Corresponding Parts of Active Sulfur
0	0
1.5	0.2
3.0	0.4
4.5	0.6
6.0	0.8
7.5	1.0
15	2.0
22.5	3.0
30	4.0
37.5	5.0

In order for vulcanization to take place, 5 per cent of zinc oxide was added to each mixture. All mixtures were milled for the same lengths of time, and all were vulcanized for 10 min. at 120° C.; this is the optimum combination for an industrial mixture containing tetramethylthiuram disulfide alone. The sample containing 1.5 parts of disulfide was too soft, whereas that containing 3 parts was fully vulcanized.

In measuring the oxidizability of the vulcanized samples, samples containing 1 gram of rubber were employed (see Figs. 18 and 18a).

Judged by the curves in Fig. 18a, the oxidizability appears to be a function of the proportion of tetramethylthiuram disulfide, although at about 15 parts per 100 parts of rubber a plateau is reached, beyond which larger proportions of the disulfide show no significant additional effect. Furthermore, as with mixtures containing sulfur alone or sulfur and a non-sulfur accelerator, the sample which was heated without tetramethylthiuram disulfide oxidized more rapidly than the samples containing from 0 to 5 parts of disulfide. Again therefore, a sort of antagonism appeared between the proöxygenic effects of simple heating and the effect of vulcanization at its initial stage.

If, in view of the facts above, it is assumed that the percentage of combined sulfur increases with the percentage of tetramethylthiuram disulfide added, it must be concluded, as was done before for mixtures containing free sulfur, that the oxidizability does not continue to increase indefinitely with increase in the proportion of polyprene sulfides, but that it tends towards a limiting value.

Finally, attention should be called once more to the existence of a minimum oxidizability, which doubtless is magnified in the present case by the distinct, though mild, antioxygenic property of tetramethylthiuram disulfide.[21] This retarding effect on the rate of oxidation should increase with proportion of reagent to a plateau common to all rubber antioxygens, which is reached at a point close to that corresponding to the minimum oxidizability, *viz.*, 1 to 2 per cent. From this point on, the proportion of combined sulfur governs the oxidizability, and this proportion has in its turn a maximum range of activity.

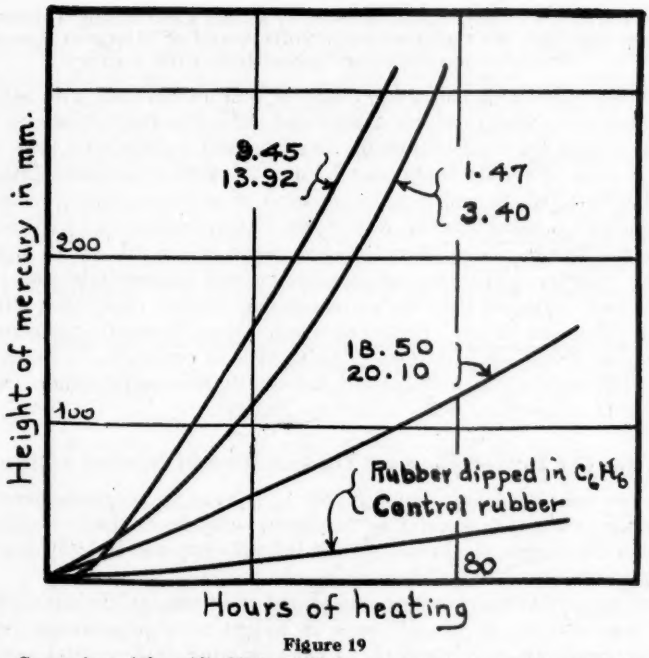

Figure 19
Comparison of the oxidizability at 80° C. of various mixtures with sulfurated accelerators with and without sulfur

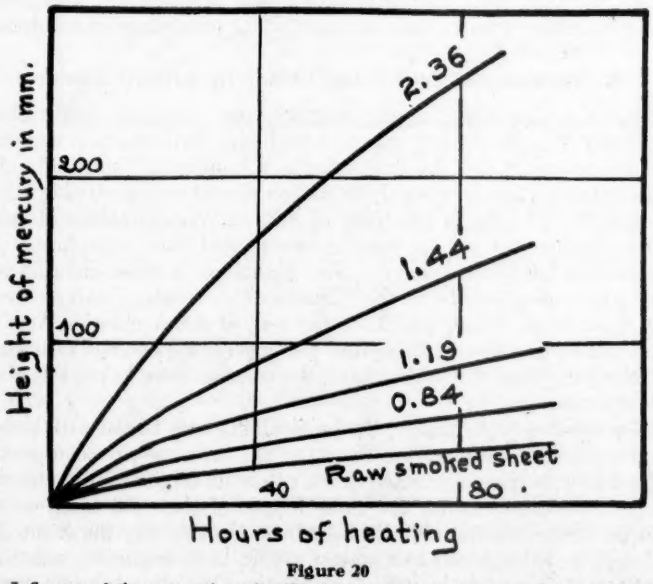

Figure 20
Influence of the proportion of sulfur in unmilled smoked sheet, vulcanized by various proportions of sulfur dioxide and hydrogen sulfide, on its oxidizability at 80° C.
The values accompanying the curves indicate the percentage increases in weight of the samples during vulcanization. These gains in weight are considered arbitrarily to be elemental sulfur

7. Comparison of the Oxidizability of Mixtures Containing Tetramethylthiuram Disulfide with and without Sulfur, and of Mixtures Containing Tetramethylthiuram Monosulfide with Sulfur

Tests of the oxidizability of these mixtures were carried out with samples prepared earlier, *i. e.*, with mixtures accelerated with tetramethylthiuram monosulfide and also with tetramethylthiuram disulfide, and containing 1 part or 2 parts of sulfur as well. Samples containing 7.5 and 15 parts of tetramethylthiuram disulfide with no auxiliary sulfur added as such were also included, since in these cases the sulfur available from the accelerator was equivalent to 1 part and 2 parts, respectively. The results of these tests are shown in Fig. 19. With 1 per cent of sulfur, the mixture containing tetramethylthiuram monosulfide was perhaps a little less readily oxidized than the corresponding mixture containing tetramethylthiuram disulfide and sulfur. But what stands out most clearly in this comparison is the superiority of the vulcanizates to which little or preferably no sulfur had been added, as is the case of the mixtures with tetramethylthiuram disulfide, particularly with moderate proportions of the latter (see Fig. 18).

8. The Influence of Cold Vulcanization by Nascent Sulfur

In this process of vulcanization[29] rubber is exposed to an atmosphere of sulfur dioxide, is then allowed to stand in air for several minutes so that the sulfur dioxide absorbed on the surface is eliminated, and is finally exposed to hydrogen sulfide in another chamber.

Smoked sheet which had not been masticated was tested. The quantity of sulfur absorbed was determined by difference in weight after preliminary drying over phosphorus pentoxide in a vacuum. In determining oxidizability, samples containing in each case 1 gram of rubber were used (see Fig. 20). Here again it was evident that with the small percentages of sulfur absorbed by this process, the oxidizability increased greatly with increase in the percentage of combined sulfur.

9. Influence of Cold Vulcanization by Sulfur Chloride

The effects of a vulcanizing agent used for many years, *viz.*, sulfur chloride, on the oxidizability of smoked sheet was next studied. Vulcanization was carried out by the Parkes process,[30] *i. e.*, by immersion in a solution of sulfur chloride in benzene. Smoked sheet, first thoroughly dried over phosphorus pentoxide in a vacuum, was immersed for 10 min. in solutions of various concentrations of sulfur chloride. After dipping, the rubber samples were dried over phosphorus pentoxide in the presence of a fat in a vacuum. The quantities of sulfur chloride which had been fixed were calculated from the differences in weight. Samples containing 1.47, 3.40, 9.45, 13.92, 18.50, and 20.10 per cent of sulfur chloride were prepared in this way. The first two of these had the general appearance of normally vulcanized rubber, the third was rather hard, the last two were as hard as ebonite and cracked fairly soon.

As in the preceding experiments, the oxidizability was tested with samples containing 1 gram of actual rubber (see Fig. 21). At the same time comparative tests were made of two samples of smoked sheet, one in its original form, the other after immersion in benzene alone for the same length of time (10 min.) as the other samples in the benzene-sulfur chloride mixtures. In this way the effect of swelling by the solvent, an effect found as a matter of fact to be negligible, was eliminated. The samples containing relatively high proportions of sulfur chloride were slightly porous, and liberated gas during their initial stage of oxidation. This led to rather serious variations in the measurements, as is manifest in Fig. 21.

CONCLUSIONS

Because of its preliminary character, the present investigation does not admit any definite conclusions. Rather, by bringing out clearly the various complications which arise in studying the oxidizability of rubber, especially when the aim is to establish a parallelism between oxidizability and the ill-defined phenomenon of aging, the investigation has shown the many difficulties in general involved in the problem.

These complications are to a certain extent attributable to the nature of the phenomenon itself which has been measured, *i. e.*, the oxidizability; but for the most part they owe their origin to the nature of the substance studied, and especially to its heterogeneous character. For these reasons the uncertainty in the re-

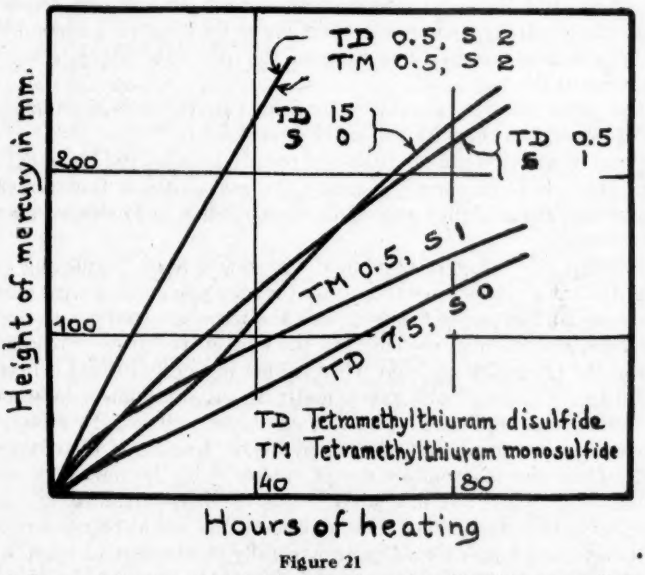

Figure 21

Influence of the proportion of sulfur chloride on the oxidizability of unmilled smoked sheet vulcanized by immersion in benzene solutions of sulfur chloride of various concentrations

The figures accompanying the curves indicate the percentage increases in weight of the samples during vulcanization. These gains in weight are considered arbitrarily to be sulfur chloride

sults is increased by vulcanization, and the more vigorous the treatment, the greater is this uncertainty. As a result, considerable fluctuation in the measurements occurred. This is the reason why, in the past as well as now, so much emphasis has has been laid on the advisability of considering as significant only relatively large differences in measurements when drawing conclusions from them.

With these reservations in mind, the facts which emerge from this opening work may be reviewed briefly.

First of all, it may be stated that, as a principle, the higher the percentage of combined sulfur, the greater is the oxidizability of rubber. In other words, it is, in a different guise, the principle accepted by the majority of technologists,[35] and which Martin[16] expressed in a particularly clear fashion, *viz.*, that the lower its state of vulcanization, the more stable is rubber.

Even if the present investigation has done no more than confirm this principle, it should not be considered as unimportant. But in view of the method of experimentation employed, the work is also a more accurate representation of the phenomena, and is, in fact, based on measurements of a property, *viz.*, oxidizability, which is simple and precise, and at the same time is very closely tied in with the origin of the transformations which rubber undergoes on aging. Hence, there is nothing surprising in the fact that the present work brings to light certain otherwise unnoticed details in more complex phenomena, such as aging, which is the indirect result of numerous reactions.

Thus, the work shows that, as a whole, combined sulfur plays an active part in the deterioration of rubber. However, in high percentages this activity changes. Above a certain upper limiting range, it becomes progressively less harmful, and the curve of oxidizability as a function of combined sulfur tends towards a plateau effect. On the contrary, below a certain lower limiting range, combined sulfur seems to behave as a protective agent, and the oxidation curve passes through a minimum close to the origin.

These two facts certainly should be confirmed by further experiments. Meantime it is of interest to consider the possible causes.

The plateau of activity can be explained readily by a partial chemical saturation by sulfur, which reduces correspondingly the reactivity of the rubber, or by a diminution in the permeability as a result of hardening, or finally by a combination of these two effects.

The minimum bad effect of combined sulfur is a more perplexing problem at first thought, if for no other reason than that it seems in conflict with current ideas; for this reason, further experiments are all the more necessary. In any event, it is no longer inexplicable if it is viewed in the light of the already recognized fact,[2] confirmed in the present work, that when rubber is merely heated it becomes more readily oxidized. There would consequently be an antagonism between the prooxygenic influence of heating and that of combined sulfur. To account for this, it need merely be assumed that, during pyrolysis, fragments of polyprene chains break away from the macromolecules of rubber, with formation of more active double bonds, *e. g.*, vinyl or conjugated. As a result the oxidizability is increased by heating. On the other hand, these double bonds would be more reactive than the other bonds, and hence would quite naturally be the first to react with sulfur. Consequently, the first effect of the combination of small quantities of sulfur would be a diminution in the oxidizability.

This special protective power shown by sulfur in small proportions may explain certain unusual instances of exceptionally long life of rubber products described by many authors from time to time, but without any convincing explanation.

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[37] These determinations were made by the indirect method, *i. e.*, the free sulfur was determined and the combined sulfur estimated by difference. The method of Caspari, with precipitation by barium chloride, was used (see reference 27).

[38] Free sulfur was determined by the method of Guppy (see reference 27), and combined sulfur was determined by nitroperchloric oxidation, with the technic of Wolesensky (see reference 28). In both cases the sulfate determination was made by the bensidine sulfate method. This method is interesting because with rubber mixtures containing talc, the silica is not rendered insoluble, and also because it makes possible a volumetric determination instead of a gravimetric one. The precision is sufficient for the problem concerned.

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The Fluorescence of Vulcanization

S. Oberto

PHYSICAL LABORATORY OF THE SOCIETÀ ITALIANA PIRELLI

Ultra-violet radiation of high intensity, in most cases from mercury-vapor lamps, has been employed in the rubber industry for two different purposes: (1) as a rapid, artificial aging test intended to duplicate under controlled conditions the surface changes on rubber brought about by sunlight, and (2) as a means of analysis by fluorescent light. On this last subject alone, there is rather extensive literature; in fact, almost every product, whether raw rubber, zinc oxide, accelerators plasticizing agents, antioxidants, or carbon blacks (by means of their extracts), has been examined by fluorescent light, and with at least some measure of success. However, it is much more of a problem to develop, from a qualitative test based on the equality or inequality of color and of intensity of two samples, a quantitative and therefore more precise method of evaluation.

An example of this is zinc oxide, which has been examined by Nagle,[1] Kirchhof,[2] Morris,[3] and Hauser.[4] Morris was able to show that the fluorescence of this substance is evident in the ash of a vulcanizate containing it, provided that the rubber sample is incinerated under carefully controlled conditions. But for a given process of manufacture, the fluorescence of a zinc oxide varies with its fineness.

Following a different line of attack, Hauser made use of a microscopic technic, and examined individual granules in fluorescent light. Here again, however, the fluorescent light from a sample of zinc oxide depends both on its impurities and on the thermal treatment it has received during manufacture, and therefore its examination by a mercury-vapor lamp is subject to the personal interpretation of the investigator. An oxide manufactured from electrolytic zinc is not fluorescent; on the other hand, two oxides with different fluorescence may have almost the same particle size and also impart the same properties to rubber.

Kirchhof,[2] Ditmar and Dietsch,[5] and Kojima and Nagai[6] have examined the fluorescence of accelerators, but even if their method of direct examination may be useful in detecting a supposed change in quality or a trace of impurities (often responsible for the fluorescence), nevertheless, when oils and antioxidants more fluorescent than accelerators are also present, it becomes impossible to identify the accelerators. The same capillary analysis by fluorescent light, first applied to rubber by Barron,[7] cannot be depended on to distinguish with any degree of certainty between two or more antioxidants and plasticizing agents.

An important factor in the analysis of rubber by ultra-violet light is the more intense fluorescence shown by overcured rubber compared with undercured rubber. The first to observe this difference was Krahl,[8] who did not seem, however, to pay any particular attention to the phenomenon.

A communication of Bruni, referred to by Cotton,[9] gives evidence that, with increase in the time of vulcanization of a rubber mixture, the fluorescence of the latter becomes progressively brighter, and that this change is greatest around the point of maximum tensile strength. Morris[3] undertook an investigation of the subject on an extensive scale, and examined rubber-sulfur mixtures, rubber-sulfur-zinc oxide mixtures, and mixtures accelerated in various ways. All the vulcanizates which had been cured for relatively long periods were strongly fluorescent, but the

most rapid changes in fluorescence did not coincide with the point of optimum state of cure. On exposure of the samples for a few minutes to sunlight or to a mercury-vapor lamp, even behind glass, the fluorescence on the surface disappeared, but a cut made it possible to examine fresh surfaces again. Morris describes the results of an examination of samples a year old.

Barron[7] mentions the fact that he carried out an extensive series of tests of various mixtures, the compositions of which are not specified, but which were vulcanized to different states, and that he obtained negative results. From this he concluded that fluorescence is useless as a criterion of the state of vulcanization. This conclusion may seem peculiar in the face of the experiments described by the earlier investigators, but there is probably a perfectly good explanation for it.

The characteristic fluorescence of rubber which appears after vulcanization can, in the light of experimental evidence obtained by the present author, be summarized in the following way.

In the case of simple rubber-sulfur mixtures containing from 3 to 8 per cent of sulfur, the intensity of the fluorescence varies with the time of vulcanization (1, 2, 3, 4, 5, . . . hours) at 143° C., and with equivalent times at other temps. By creating numerous refractive surfaces, crystallization of sulfur within a vulcanizate can alter the intensity of the light emitted and may impart to the vulcanizate an irregular spotted appearance. In such cases a brief period of heating at 100° C. will dissolve the sulfur and make it possible to examine the sample undisturbed for a reasonable length of time.

In the absence of sulfur, the fluorescent light emitted by raw rubber is not altered by raising the rubber to an elevated temperature.

When the percentage of sulfur is relatively high, *i. e.*, above 10 per cent, and semi-ebonite products are formed, the fluorescence of the vulcanized products becomes less intense again, and is of a brown-red color, resembling that of strongly oxidized vulcanizates.

Addition of zinc oxide, preferably manufactured from electrolytic zinc and therefore with no fluorescence of its own, to a rubber-sulfur mixture accelerates the changes in fluorescence to the same degree that it accelerates vulcanization. In order to bring out distinct differences between samples vulcanized for increasing times, it is advisable to utilize a geometric progression of times of vulcanization rather than an arithmetical progression, which increases dynamometrically the intervals between the initial times and shortens those between the later times.

With accelerators present, *e. g.*, diphenylguanidine and mercaptobenzothiazole, the tendency of the fluorescence to increase in intensity with increase in the time of vulcanization is still to be found. This change in intensity is, however, greater with some accelerators than with others, *i. e.*, where the mixtures lose their tensile properties more quickly and where the fillers are not exceptionally fine.

The relation between fluorescence and state of cure which was described by Bruni (*loc. cit.*), and which Morris (*loc. cit.*) could not find sufficient evidence to confirm, must be interpreted solely as indicating that in the majority of cases undercured rubber mixtures show relatively weak fluorescence, while overcured rubber mixtures show a strong fluorescence. In the case of simple rubber-sulfur mixtures this fluorescence of overcured rubber is greenish, and in the case of accelerated mixtures is green-yellow. When overcuring is excessive, a yellow fluorescence is frequently manifest.

Photographing of vulcanized rubber in fluorescent light offers no particular difficulties; it is necessary, of course, to use objectives of small aperture, and yellow screens to eliminate all ultra-violet radiation, and to expose for 30 min. or longer,

depending on the nature of the sample. Orthochromatic plates are quite satisfactory, even if panchromatic plates are seemingly more adapted for the purpose.

The photograph in Fig. 1, made in fluorescent light, shows four test-specimens which had been vulcanized for 4, 8, 12, and 20 min. (from left to right in the photograph) at 143° C. The composition of the mixture was:

Rubber	100
Sulfur	3
Tetramethylthiuram disulfide	0.5
Zinc oxide	5
Calcium carbonate	20

The photograph in Fig. 2 shows the same test-specimens photographed in natural light. They all appear the same, and it is impossible to detect which has been vulcanized for the shortest time and which has been vulcanized for the longest time.

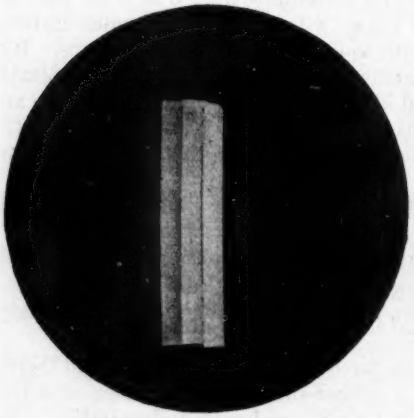

Figure 1

Photograph, taken in fluorescent light, of samples of rubber vulcanized for various times. With increase in the time of vulcanization there is an increase in brightness

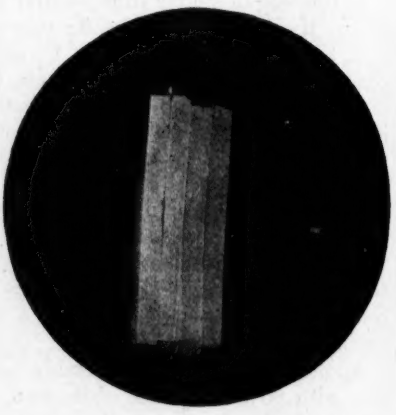

Figure 2

Photographs of the samples shown in Fig. 1, but taken in natural light. In this case there is no increase in brightness with increase in the time of vulcanization

On the other hand, by fluorescent light the individual states of cure are readily distinguishable, and this would be still more evident if the samples were in different order.

Hundreds of rubber mixtures, when not heavily loaded with fluorescent ingredients, such as lithopone, certain types of zinc oxide and organic coloring agents, or with opaque ingredients, *e. g.*, more than 2 per cent of carbon blacks, have been found to show changes in fluorescence similar to those illustrated in Figs. 1 and 2.

When there is a deficiency of zinc oxide, *i. e.*, only 1 per cent or a little more, and no other filler is present, the progressive disappearance of this zinc oxide during vulcanization results in a progressive change in transparency and general appearance of the vulcanizates, which is evident even in natural light. The changes in fluorescence do not, however, bear any relation to these changes in transparency, since these changes are also evident with very high loadings of zinc oxide, calcium carbonate, titanium dioxide, blanc fixe, etc.

It is interesting that in the initial stages of vulcanization, the fluorescence is relatively feeble, and that with increasing vulcanization it becomes progressively

brighter. This initial stage, which usually passes unobserved, has a certain theoretical interest, and only the comparatively rapid increase in fluorescence as vulcanization progresses can account for the fact that there has been no comprehensive study of the phenomenon.

If a partially vulcanized rubber mixture is extracted with acetone, and is then heated again so that vulcanization continues, the fluorescence changes progressively in the same way as if the mixture had not been extracted. Consequently, the first vulcanization must have almost reached the optimum point for the mixture; or expressed in more exact terms, the increased brightness of the fluorescence of overcured rubber does not depend on the increased percentage of combined sulfur, but indicates a change in character of the vulcanized rubber already formed.

That there is no relation between the intensity of the fluorescence and the proportion of combined sulfur is also evident in the fact that vulcanizates containing less than 1 per cent of total sulfur, but high percentages of accelerator (*e. g.*, 3 per cent of diphenylguanidine), and vulcanized to the point of reversion, show extremely bright fluorescence. On the contrary, mixtures vulcanized with low percentages of sulfur and at a low temperature, *i. e.*, below 100° C., and mixtures vulcanized with tetramethylthiuram disulfide in the absence of sulfur, show no change in fluorescence as vulcanization progresses. Mixtures vulcanized with tetramethylthiuram disulfide alone also show the most pronounced plateau effect when tested mechanically, and are particularly stable when heated. It is probable that Barron examined mixtures of this last type, which includes many latex mixtures, and for this reason did not encounter the phenomenon described by Bruni and by Morris.

At temperatures of liquid air, the fluorescent light from vulcanized rubber does not show any particular characteristics which seem to warrant a study under these conditions. The widest bands of which it is composed do not become appreciably narrower, while at the same time zinc oxide and certain antioxidants give off a troublesome bright phosphorescence.

The fluorescent light of vulcanization has a peculiar characteristic which is common to the fluorescent light of certain types of raw rubber and also to latex rubber; when the rubber is stretched sufficiently its fluorescent light is strongly polarized. If birefractive fillers are present, the state of polarization of the light emitted from below the surface (for several hundredths of a millimeter) is disturbed, but when the mixture is rendered opaque by the addition of a little carbon black, fluorescent light is emitted only from the surface of the rubber, and its polarization can be examined without this disturbing effect.

It can be demonstrated in this way that polarization first appears at an elongation of approximately 100 per cent, *i. e.*, an elongation of the same order of magnitude at which x-ray interferences indicate the formation of a crystalline structure. At higher elongations, polarization becomes almost complete.

Morris in the work already cited (*loc. cit.*) mentions the fact that the fluorescence of vulcanized rubber disappears after the rubber has been exposed to sunlight or to a mercury-vapor lamp. As a matter of fact, this loss of fluorescent power occurs so quickly that, in a comparison of the fluorescence of two vulcanizates, it is always necessary to examine fresh surfaces, *e. g.*, fresh cuts. With the fluorescent microscope, in which the ultra-violet beam is highly concentrated on the area under examination, the fluorescence of vulcanization disappears within a period of even a few seconds. This disappearance is not attributable to oxidation, because it occurs when the rubber is in an atmosphere of carbon dioxide or is in a vacuum.

The fluorescence exhibited by vulcanized rubber is also excited by cathode rays,

but this method seems to have no advantage experimentally over that which utilizes ultra-violet radiation for excitation. Moreover, with cathode rays, the fluorescence gradually becomes weaker, so that to observe the fluorescent effect, over an extended period of time, the surface must be renewed.

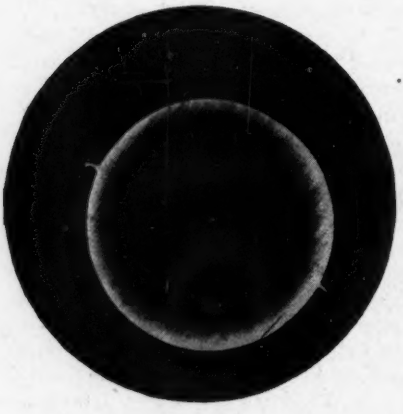

Figure 3

Photograph, taken in fluorescent light, of a rubber ball, 6 cm. in diameter, which is undercured. A narrow zone around the outside is well vulcanized, the inside is vulcanized very little

Figure 4

Photograph of a rubber stopper. Here, too, the outside part is well vulcanized, the inside insufficiently vulcanized

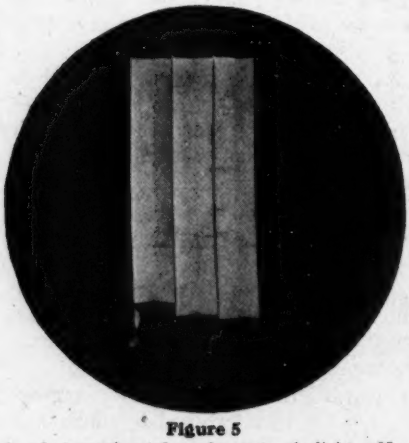

Figure 5

A photograph, taken in natural light. No differences between the two rubber mixtures, of which each of the three separate discs are composed, are evident in the photograph

Figure 6

A photograph, taken in fluorescent light, shows differences between the two component parts of each of the three vulcanized discs shown in Fig. 5

Finally, it should be remarked that when Neoprene is vulcanized without sulfur, in other words when the only change is an increase in the degree of polymerization, there is a similar change in fluorescence. In this case the change is not pronounced. but it is nevertheless quite distinct.

The fluorescence which is so characteristic of the vulcanized state offers a method which, though not very sensitive, is simple and quick for judging the state of vulcanization of a product, almost without touching it. The fluorescent effect is of particular service in making it possible to obtain at one glance an idea of the homogeneity of vulcanization of an object of large size.

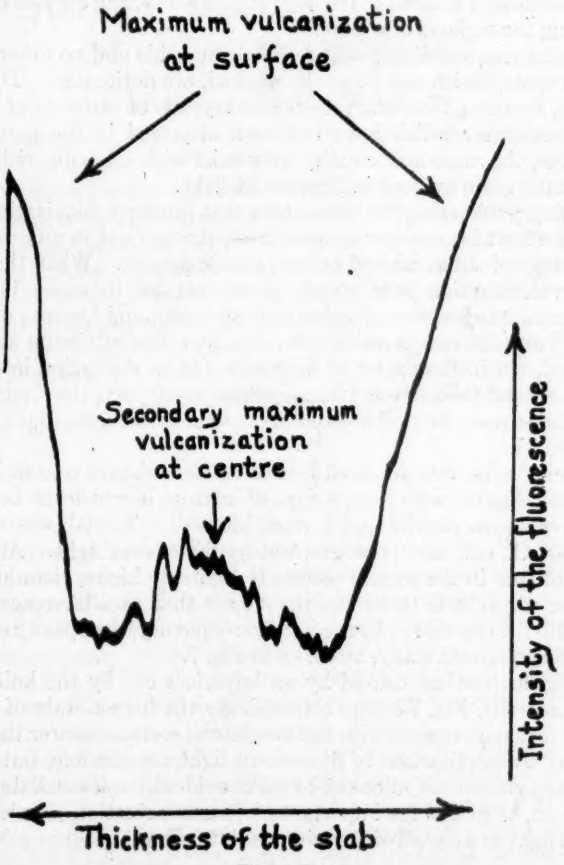

Figure 7

Examination, with a microphotometer, of a section of a thick slab of rubber prepared from a mixture having a high heat of vulcanization

The photographs in Figs. 3 and 4, taken by fluorescent light, illustrate cases which are a little unusual but nevertheless are significant—a rubber sphere and a rubber stopper, each about 6 cm. in diameter, which have been vulcanized for too short a time. Whereas all of the central parts are non-fluorescent and undercured, the outer regions show a bright fluorescence and are already overcured.

Formerly, when rubber mixtures generally contained high percentages of sulfur, the blooming of the sulfur gave direct evidence of the lower state of cure of the inner regions; however, the low percentages of sulfur used today make it impossible to

judge the state of cure in this manner, except in a far less precise way, and only after far more delay, than does an examination by fluorescent light.

The photographs in Figs. 5 and 6, that in Fig. 5 taken in natural light, that in Fig. 6 in fluorescent light, represent three small discs, each made from two different rubber mixtures. The presence of different mixtures is hardly discernible in Fig. 5, whereas it is very evident in Fig. 6. The differing states of vulcanization of each pair of mixtures is evident in the most striking way, and various effects are also to be seen along the surfaces of contact.

In rubber mixtures containing only a little zinc oxide and no other fillers, small, circular, dark spots, which can be easily cracked, are noticeable. These are zones of higher cure, resulting from the presence of crystals of sulfur or of agglomerated granules of accelerator which have not been dispersed in the normal way. In loaded mixtures, the same abnormality may exist without being visible in natural light, yet become quite evident in fluorescent light.

In a preceding publication,[10] it was shown that during vulcanization all types of mixtures evolve heat in measurable quantities, the amount in any case depending on the percentage of sulfur and on other variable factors. When the evolution of heat during vulcanization is relatively great, notable increases in temperature above the normal temperature of vulcanization occur, and because of these higher temperatures vulcanization is accelerated locally. The minimum state of cure is therefore found, not in the center of the block, but in the region intermediate between the center and the surface. In a corresponding way, the fluorescence, while brightest at the surface, shows a secondary, more or less intense maximum at the center of the block.

A slab 16 mm. thick was prepared from a rubber mixture containing 7 per cent of sulfur and accelerated with lime, a type of mixture in which the heat of vulcanization is evolved most rapidly and is most intense. The slab was vulcanized for 14 min. at 160° C., cut, and photographed by fluorescent light. Although to the eye the state of cure in the central section is distinctly higher than in the adjacent regions, nearer the outside there was the chance that this difference could not be reproduced with the necessary clearness. Consequently, the opacity of the negative was reproduced photometrically, as shown in Fig. 7.

Disregarding fluctuations caused by an imperfect cut by the knife used (as in Figs. 3 and 4 as well), Fig. 7 shows convincingly the higher state of vulcanization in the central region compared with the two lateral sections nearer the surface.

Numerous other applications of fluorescent light are possible, but the examples which have been chosen are sufficient to make evident the immediate results which may be obtained, as well as the importance, of an examination of vulcanized rubber by fluorescent light as a means of studying its state of cure.

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The Influence of the Crystallographic Transformation of Sulfur on the Course of Vulcanization

J. Arvid Hedvall and Atle Larsson

Laboratory of Industrial Chemistry, Chalmers Technical College, Göteborg, Sweden

One of the authors has already been able to show, with the support of a large number of cases, that whenever a solid substance undergoes a change in its structure during a reaction, the reactivity of the substance increases considerably.[1] Naturally this principle also holds true in reactions in which a solid substance reacts, not with another solid substance, but with a liquid or with a gas.

This behavior of crystalline substances may be accounted for by an increase in their reactivity resulting from the reduced heat of dissociation during the period of transformation from one form to another. The effect of changes in energy, as judged by processes which depend on structural changes within the crystal, leads directly to the following expression for the velocity:

$$Ae^{-\frac{q}{RT}}$$

where q is the so-called heat of dissociation mentioned above, R is the gas constant, T is the absolute temperature, and A is a material constant which is independent of temperature but does depend on the particle size, surface area, etc.

Several years ago it was shown[2] that the velocity of solution and the oxidizability of sulfur increase greatly during the transformation process: $S_{\text{rhombic}} \rightarrow S_{\text{monoclinic}}$, which takes place at 95–96° C. In view of this it seemed of interest to ascertain whether a corresponding effect is recognizable during the combination of rubber with sulfur in the solid state in vulcanization.

In the following discussion, the method by which the problem was attacked and the results of the experiments are covered in a very brief way.

In each series of experiments, 100 grams of pale crepe were first masticated for 15 minutes to a suitable plasticity; and the accessory ingredients were then milled into the rubber on an ordinary roll mill during a period of 20 minutes. Any incipient vulcanization which might take place during this process was avoided by proper cooling.

As a means of comparison, two different mixtures, designated below as I and II, were prepared by this technic.

	I	II
Pale crepe	100	100
Sulfur	6	10
Vulkazit P	1	..
Vulkazit P extra N	..	1
Stearic acid	2	5
Zinc oxide	10	30
Whiting	10	50

After a little practice, it was found possible to obtain these mixtures repeatedly with the same properties.

In all cases samples of the same size (10 cm. long, 5 cm. wide, 0.5 cm. thick) were vulcanized in an accurately controlled thermostat for 45 minutes at the desired temperature. The vulcanized samples were then chilled in ice-water and ground fine between tight, cooled mill rolls.

To determine the percentage of uncombined sulfur, 3 grams of each fine-ground sample were extracted for 24 hours with acetone in a Soxhlet apparatus, and the sulfur was determined as barium sulfate. The following table, which gives the analytical data of two parallel series of experiments, shows the precision of the work, and the curve in the diagram gives the same results in graphical form.

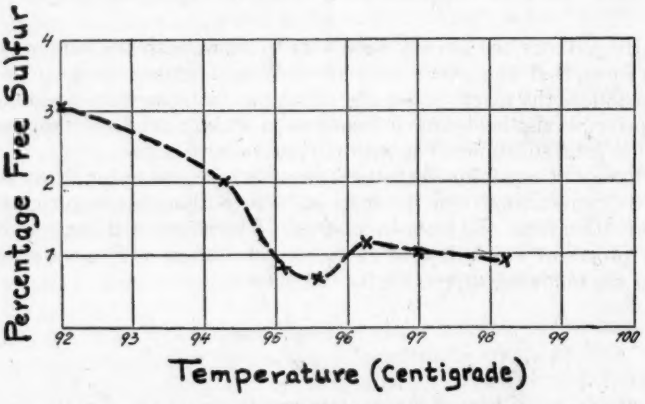

Figure 1

Temperature (° C.)	Percentage of Uncombined Sulfur in Two Parallel Experiments A	B	Average
92	3.05	3.10	3.07
94.3	1.98	2.05	2.01
95.1	0.82	0.85	0.83
95.6	0.71	0.75	0.73
96.2	1.22	1.28	1.25
97.0	1.10	1.09	1.10
98.2	0.97	1.01	0.99

These measurements show clearly that the transformation effect sought for, *i. e.*, an increase in reactivity of a solid substance during its transformation into another structural form, is manifest in the combination of sulfur with rubber during vulcanization. In other words, the rate of combination of sulfur with rubber passes through a relative maximum precisely at the point of transformation of sulfur from one form to another. On the curve shown, this maximum rate is evident by a relative minimum point on the free sulfur curve. This minimum appears in varying degrees of sharpness with different rubber mixtures.

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Vulcanization of Rubber in the Presence of meta-Dinitrobenzene

J. M. Wright and B. L. Davies

Department of Chemistry and Rubber Technology, Northern Polytechnic, London

Part I. The Formation of Soft Vulcanizates*

Since Ostromislensky (*J. Russ. Phys. Chem. Soc.*, **49**, 1456 (1916)) claimed that vulcanization of rubber in the presence of *m*-dinitrobenzene entailed the addition of oxygen to the rubber molecule, it has been suggested that this form of vulcanization may be the oxygen analog of ordinary sulfur vulcanization. Blake (*Ind. Eng. Chem.*, **22**, 740 (1930)), however, extracted vulcanizates with acetone and determined the nitrogen content. If it were assumed that the unextractable nitrogen was combined with the rubber, the figures indicated that the chemical reaction was monomolecular, and in explanation it was suggested that consecutive reactions occurred, one of which was slow. The vulcanizate was concluded to be an additive compound of the vulcanizing agent with the rubber.

Objects and Technic.—The objects of the present work were to answer two questions: (1) what are the reactants, and (2) in what manner do they react? It was hoped with the simplest binary mixtures to find what were the essential ingredients, and to proceed to increasingly complex mixtures to discover the roles of the various accessory substances.

By vulcanization in solution it was found that the examination of the final reaction mixture was facilitated. The mixes were therefore dispersed in technical xylene, of boiling point 140° C., and vulcanized by boiling. At a particular stage, the rubber became insoluble, and the time required to arrive at this stage was a characteristic of the mix and was taken to be proportional to the rate of reaction.

Binary Mixtures.—Using rubber previously purified by acetone extraction or by fractional precipitation from benzene, it was found that a mixture containing only one other component did not vulcanize normally, although small quantities of insoluble residue were obtained as described in Table I.

Table I

Substance Added to Rubber Solution	Result of Boiling
m-Dinitrobenzene	After 200 hours a very small quantity of a hard black substance remained
Lead monoxide	Slight rubber-like residue after 200 hours
Lead dioxide	Similar to above but larger quantity
Barium monoxide	Small amount of soft rubber-like residue after 200 hours
Barium peroxide	Appreciable amount of insoluble rubber after 24 hours
Stearic acid	Solution darkens on long boiling but no residue after 200 hours
Lead oleate Lead stearate Barium oleate or Barium stearate	Effect similar to stearic acid
Phenol	Trace of rubber separated after 10 min. and subsequently redissolved. No permanent residue after 200 hours

* Part I incorporates work described by J. M. Wright in an essay which was awarded the Dawson Silver Medal by the Institution of the Rubber Industry in 1937.

It was thus shown that *m*-dinitrobenzene was incapable of vulcanizing purified rubber, even on prolonged heating.

The residues were freed from as much entrained oxide as possible by washing with mixed ether and dilute hydrochloric acid, incinerated, and the metal estimated gravimetrically. One gel was found to contain 7.2 per cent of lead and another, 9.2 per cent of barium. These figures were not repeatable, however, and it was concluded that the metal did not combine with the rubber.

Tertiary Mixtures.—Mixtures of extracted rubber, *m*-dinitrobenzene, and a third substance yielded vulcanizates only when the third substance was a metallic oxide. The time of heating was very long and was reduced to a remarkable extent by the addition of a little fat acid or by using technical rubber, as shown in Table II.

Thus three substances take part in the vulcanization of the rubber, namely, *m*-dinitrobenzene, a metallic oxide, and a fat acid. It has been shown elsewhere (Wright, *Trans. Inst. Rubber Ind.*, **12**, 189 (1936)) that only basic oxides are capable of exerting a marked influence.

The Action of the Accessory Substances.—It is certain that the fat acid and the basic metallic oxide combine at vulcanizing temperatures to produce water and a soap which is probably rubber-soluble. It must next be determined, therefore, whether the soap or the water can act in place of the two accessories to vulcanization. When added to the purified rubber base mix, the stearates and oleates of lead and barium showed no vulcanizing effect after long periods of boiling. Crystalline aluminum sulfate, containing 18 molecules of water of crystallization, was used as a steady source of water. The mix vulcanized satisfactorily in $1\frac{1}{2}$ hours, whereas the control mix containing the anhydrous salt had not gelled after 10 hours' boiling.

TABLE II

Mix: Extracted Rubber + *m*-Dinitrobenzene	Effect of Boiling
+ litharge	Small quantity of gel after 22 hours
+ barium monoxide	Small quantity of gel after 75 hours
+ fat acids	No gel after 200 hours
+ phenols	No gel after 200 hours
+ litharge + stearic acid	Gel after 4 hours
+ litharge + oleic acid	Gel after 2 hours
Mix: Pale Crepe Rubber + *m*-Dinitrobenzene	
+ litharge	Gel after $4\frac{1}{2}$ hours
+ litharge + stearic acid	Gel after $3\frac{1}{2}$ hours
+ litharge + oleic acid	Gel after $2\frac{1}{4}$ hours

The acceleration by water was confirmed by means of physical tests on vulcanizates prepared by more normal procedure. Very thin sheets of a mix consisting of pale crepe rubber 100, litharge 10, *m*-dinitrobenzene 5, were dried in a vacuum for a week. To one portion 1 per cent of water was added, and samples of each were vulcanized in the press for various periods and their physical properties examined by means of the Schopper tensile machine.

At the same time, to other portions of the dried mix were added 1 per cent of nitrobenzene, of methyl cyclohexanone, and of lead hydroxide. In this way it was hoped to draw conclusions regarding the action of water as a solvent for *m*-dinitrobenzene. The results, shown in Table III and in Figs. 1 and 2, demonstrate clearly the accelerating influence of water. No such effect was shown by the other liquids, and it was concluded therefore that the action of water is not simply that of a solvent.

TABLE III

Mix	Min. Vulcanization at 141° C.	Modulus (Lb. per Sq. In.) at 300% Elongation	Modulus (Lb. per Sq. In.) at 600% Elongation	Tensile Strength Lb. per Sq. In.
"Dry" base	15	62	165	170
	30	108	265	677
	45	123	335	1520
Base + 1% water	15	130	375	1925
	30	175	620	1500
	45	200	710	1500
Base + 1% lead hydroxide	15	50	60	160
	30	100	225	110
	45	117	340	1265
Base + 1% methyl cyclohexanone	15	55	160	450
	30	110	280	1100
	45	117	300	1400
Base + 1% nitrobenzene	15	65	170	200
	30	110	250	1100
	45	115	290	1150

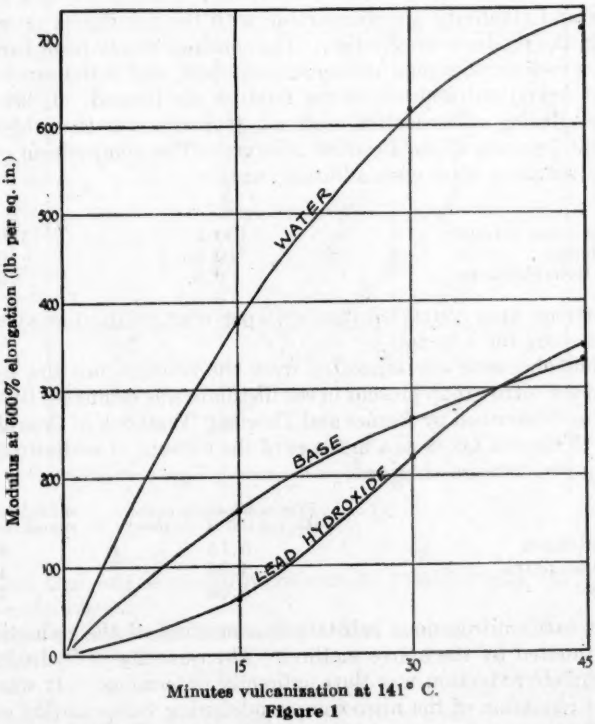

Figure 1

The Reactions of m-Dinitrobenzene in Aqueous Media.—It must be supposed that water takes part in the chemical reaction, and it was therefore decided to examine the reaction products of *m*-dinitrobenzene with water, particularly in the presence of bases.

Samples of the nitro compound were heated under various conditions and the products examined. Only in an alkaline medium did reduction occur. The results

are compared in Table IV with observations made on vulcanization reaction mixtures. The products identified in the absence of rubber agree with the observations of de Bruyn and Blanksma (*Rec. trav. chim.*, **20**, 115, 141 (1901)).

TABLE IV

1 *m*-Dinitrobenzene + Dilute HCL	2 *m*-Dinitrobenzene + Distilled Water	3 *m*-Dinitrobenzene + Lead Hydroxide in Water	4 During Vulcanisation in Solution	5 *m*-Dinitrobenzene in 4 *N* Sodium Hydroxide
No action	2,4-Dinitrophenol	Ammonia	Vulcanizate	Ammonia
		Oxalate	Ammonia (trace)	Oxalate
		Partial reduction, products of *m*-dinitrobenzene	Oxalate (trace)	Partial reduction products of *m*-dinitrobenzene
		Carbon dioxide (trace)	Partial reduction, products of *m*-dinitrobenzene	Carbon dioxide (trace)
		Lead nitrate (trace)	Lead nitrate (trace)	Nitrite and nitrate

There is a marked similarity between Columns 3, 4, and 5, showing that when the temperature and alkalinity are comparable with the conditions prevailing in the rubber stock, the products are Similar. The conclusion may be drawn that during vulcanization *m*-dinitrobenzene undergoes reduction, and at the same time smaller quantities of oxidation products of the mixture are formed. It seems probable therefore that during vulcanization oxygen is transferred to the rubber.

Quantitative Analysis of the Reaction Mixture.—The composition of a mix, determined by weighing after each addition, was:

	Parts by Weight	
Pale crepe rubber	100.2	100
Litharge	10.4	10.38
m-Dinitrobenzene	9.8	9.78

Weighed portions were converted into a 10-per cent solution in xylene and vulcanized by boiling for 4 hours.

Free *m*-dinitrobenzene was separated from the reaction mixture by steam distillation, and the nitro-group present in the distillate was estimated by the stannous chloride method described by Barnet and Thorne ("Textbook of Organic Analysis," **1921**, 151). This was taken as a measure of the amount of *m*-dinitrobenzene, and the following results were obtained:

	Free *m*-Dinitrobenzene (G. per 100 G. Rubber)	*m*-Dinitrobenzene Consumed (by Difference)
First batch	5.15	4.63
Second batch	4.92	4.86
Mean	5.03	4.75

The non-volatile nitrogenous substances consisting of the reduction products were also estimated by the above method. The quantity of hydrogen necessary for their complete reduction was thus indirectly determined. It was found that the degree of reduction of the nitro compound during vulcanization corresponded to a loss of 0.64 gram oxygen per 100 parts of rubber, which agrees satisfactorily with the figure 0.68 calculated on the assumption that the *m*-dinitrobenzene consumed during vulcanization was reduced to 3,3-dinitroazoxybenzene.

The ammonia and volatile amines evolved during vulcanization were absorbed in acid, and estimated volumetrically. Treating this as ammonia, 0.087 gram was formed per 100 grams of rubber. This reduction was equivalent to a loss of 0.164 gram of oxygen per 100 grams of rubber.

Oxalate present after vulcanization was separated as the calcium salt, dissolved in acid, and estimated by titration with potassium permanganate. The amounts of oxygen mentioned below are based on the supposed oxidation of *m*-dinitrobenzene to oxalic acid, although the existence of such a change is not proved.

	Oxalic Acid Formed	Oxygen Needed	
First batch	0.015 g.	0.010 g.	per 100 g. rubber
Second batch	0.016 g.	0.011 g.	

Further examination indicated a trace of lead nitrate, and absence of nitrite and carbon dioxide. The metallic oxide appeared unchanged in color, and it was assumed that it underwent no permanent oxidation. Attempts to separate it completely from the rubber were unsuccessful.

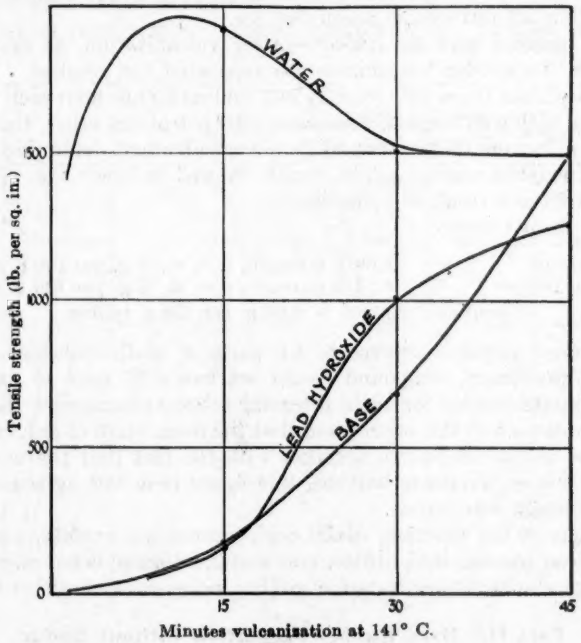

Figure 2

It is believed that loss of *m*-dinitrobenzene by volatilization was small and did not influence the results.

The Oxygen Combined with the Rubber.—The analytical results may now be summarized.

	Oxygen Change (G. per 100 G. Rubber)
From formation of ammonia and amines	0.16 given up by *m*-dinitrobenzene
From partial reduction of nitro compound	0.64 given up by *m*-dinitrobenzene
Total oxygen given up	0.80 given up by *m*-dinitrobenzene
From formation of oxalic acid (if from *m*-dinitrobenzene)	0.01 taken up by *m*-dinitrobenzene

There is little doubt that the first item consisted mainly of amines, and consequently the oxygen value is somewhat doubtful. There was, however, a small

quantity of ammonia, and it is probable that a small quantity of *m*-dinitrobenzene was degraded, the nitrogen residue forming ammonia and the carbon-hydrogen structure being oxidized to oxalic acid. There is thus at least 0.64 gram of oxygen unaccounted for, and this may reasonably be taken to have combined with the rubber.

As a check on these figures, the distribution of nitrogen as calculated from the analytical results may be noted. Thus:

Free *m*-dinitrobenzene	0.84 g. nitrogen
Ammonia, etc.	0.07 g. nitrogen
Partial reduction products considered as azoxy compound	0.75 g. nitrogen
Total	1.66 g. nitrogen

The total amount of *m*-dinitrobenzene in the mix was 9.78, containing 1.63 grams nitrogen. Thus all nitrogen is accounted for.

Nitrogen Combined with the Rubber.—After vulcanization, as described, of a further batch, the swollen vulcanizate was separated and crushed. The product was then treated four times with fresh xylene, boiling for one hour each time. After washing twice with cold benzene and twice with petroleum ether, the vulcanizate was dried in a vacuum desiccator and its nitrogen content determined by a modification of Kjeldahl's method. The results showed in every case an increase in nitrogen content as a result of vulcanization.

The mean results were:

Vulcanizate	0.66% nitrogen, *i. e.*, 0.79 g. per 100 g. rubber
Original rubber	0.13% nitrogen, *i. e.*, 0.13 g. per 100 g. rubber

Combined nitrogen = 0.66 g. per 100 g. rubber

This combined nitrogen represents 4.0 parts of *m*-dinitrobenzene, which on reduction to the azoxy compound would set free 0.57 part of oxygen. This would remain unaccounted for in the foregoing scheme of analysis. In view of the involved operations and the assumption that the mean state of reduction is represented by the azoxy compound, together with the fact that the determinations were carried out on duplicate batches, this figure is in fair agreement with the figure 0.64 actually determined.

The products of the reaction, oxalic acid, ammonium oxalate, azo and azoxy compounds, lead nitrate, lead nitrite, and also 2,4-dinitrophenol all proved to be incapable of producing vulcanization of rubber, either with or without litharge.

Part II. Hard Rubber Formation without Sulfur

In the course of work on the vulcanization of rubber by nitro compounds it has been repeatedly found that hard rubber cannot be obtained. Bunschoten (*Kolloid-Z.*, **23**, 25 (1918)) and more recently Blake (*Ind. Eng. Chem.*, **29**, 866 (1937)) have definitely asserted that ebonite cannot be produced with this reagent. Ostromislensky ("Chemistry and Technology of Rubber," New York, **1937**, 273), in discussing the use of 8 to 10 per cent of nitro compound and the poor aging properties of the soft vulcanizates produced, considers it possible to prepare a chemical analog of ordinary sulfur ebonite, but that "hard rubber in the literal sense cannot be obtained in this way."

In view of the influence of water on the production of soft vulcanizates, as described in Part I, it was thought possible that in the presence of moisture and sufficient nitro compound, the vulcanization reaction might proceed further and form a product resembling ebonite. If so, it would be of interest to examine the nature of the product and the conditions of its formation.

Preliminary Experiments.—A mixture consisting of 100 parts of pale crepe rubber, 150 parts of *m*-dinitrobenzene, and 10 parts of litharge was saturated with water on the laboratory mill and the slab placed in a shallow dish. It was covered with water containing excess of *m*-dinitrobenzene and litharge, and the whole heated in steam at 141° C. After $1^1/_2$ hours, the vulcanizate was very tough, resembling a rubber-sulfur semi-ebonite, and after 3 hours' heating a rigid product was obtained. It was very hard and rather brittle; it could be sawed, filed, and polished to give a good black color. It was apparently unchanged after 6 weeks' aging in the Geer oven at 80° C., and it was concluded that a product similar to sulfur-cured hard rubber had been obtained.

As water has been shown to accelerate soft rubber vulcanization, it was reasonable to expect more rapid formation of hard rubber in humid conditions. To confirm this view, a similar batch was halved. To one portion (A) 5 parts of water were added on the mill, portion B receiving no further milling. Samples of each portion

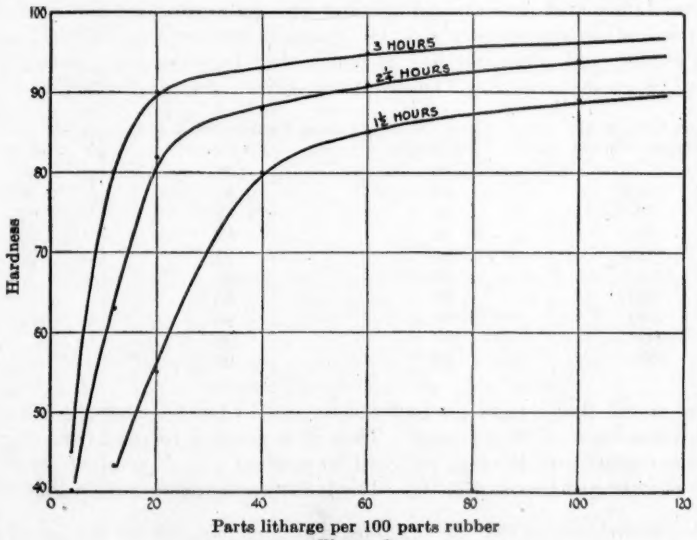

Figure 3

were then vulcanized in the press. After 1 hour at 150° C. both had reached the soft rubber stage, though sample A was much tougher. After 4 hours, sample A was hard and rigid, although B was still flexible. Thus it was confirmed that water accelerated the cure. Alternative and more convenient methods of supplying moisture were therefore sought.

Use of Damp Fillers.—By the use of absorbent fillers previously wetted, it was hoped that the difficulties associated with the direct addition of water on the mill would be overcome. A paste consisting of 20 parts of bentonite clay and 5 parts of water was mixed with the basic stock, but dispersion was difficult and the properties of the vulcanizate were impaired. Vulcanization proceeded rapidly, however, 1 hour at 150° C. being sufficient to produce a rigid product, which had a tensile strength of 2000 lb. per square inch. Similar results were obtained, using wood flour, although vulcanization was less rapid, probably due to the retarding effect of resins (Wright, *Trans. Inst. Rubber Ind.*, **12**, 183 (1936)).

Production of Water in Situ.—A convenient method of adding water is to include in the mix an acid and a base which would react at or below vulcanizing temperatures and so liberate water. Litharge, already present, served as the base. It was necessary, however, to use only weak acids, together with excess of base, as *m*-dinitrobenzene is not reduced in acid solution. Stearic and oleic acids were therefore tried. Mixes as described above, with the addition of 10 parts of acid, were heated for 5 hours at 141° C. Each vulcanizate was hard but relatively weak, particularly that containing oleic acid.

It has been established then that hard rubber resembling ordinary ebonite can be prepared from mixtures containing 150 parts of *m*-dinitrobenzene per 100 parts of rubber, together with litharge and water, by heating for reasonable times at usual vulcanizing temperatures. It was now possible to examine quantitatively the conditions of formation of the hard product.

The Effect of the Metallic Oxide.—To portions of a mix containing 150 parts of *m*-dinitrobenzene per 100 parts of pale crepe rubber, 1.5 parts stearic acid, and 1.5 parts of oleic acid, various quantities of litharge were added and vulcanization was carried out in the press at 153° C. Samples were removed at various times, rapidly chilled, and, after standing 24 hours, their hardness was measured by the standard Shore instrument. The results are shown graphically in Fig. 3.

Parts Litharge per 100 Parts Rubber	Hardness Figures after Curing for		
	1½ Hours	2¼ Hours	3 Hours
4	40	40	45
12	45	63	80
20	55	82	90
40	80	88	93
60	85	91	95
100	89	94	
240	94	95	
480	94.5	96	
800	94	96	
1000	95	96	

It was found that a rigid product was attained when the Shore instrument registered a hardness of 90 per cent. Thus it is possible to read from Fig. 1 the minimum quantity of litharge required to produce a hard product after various periods of vulcanization at 153° C. The following figures are recorded:

For 1½ hours' cure at 153° C.	120 parts litharge required per 100 parts rubber
For 2¼ hours' cure at 153° C.	50 parts litharge required per 100 parts rubber
For 3 hours' cure at 153° C.	20 parts litharge required per 100 parts rubber

Further, by plotting these values (Fig. 4) it is possible to read intermediate values and also to see that the minimum quantity of litharge which is capable of yielding a hard product is small, being of the order of one part by volume.

The Minimum Quantity of m-Dinitrobenzene.—To determine the extent to which the *m*-dinitrobenzene content could be reduced below the 150 parts already shown capable of yielding a rigid product, fixed quantities of metallic oxide and wood meal filler were used. The base mix consisted of 100 parts of pale crepe rubber, 40 parts of litharge, 50 parts of wood meal wetted with 2 parts of water. Aliquot parts were compounded with various quantities of *m*-dinitrobenzene, and all were vulcanized together in the press for 2½ hours at 153° C. The hardness figures were not as sensitive an index of the properties of the samples as a bending test by hand. The loading caused initial hardness which masked changes due to increased state of cure.

Parts *m*-Dinitrobenzene per 100 Parts Rubber			
50	Increasing toughness	110	Fractured on bending
60		120	
70		130	
80		140	Rigid and brittle
90			
100			

From hand tests it was evident that samples of the first group were very sensitive to temperature change and resembled semi-ebonite. Those of the second group were tougher and the last sample was hard and brittle. After further heating for

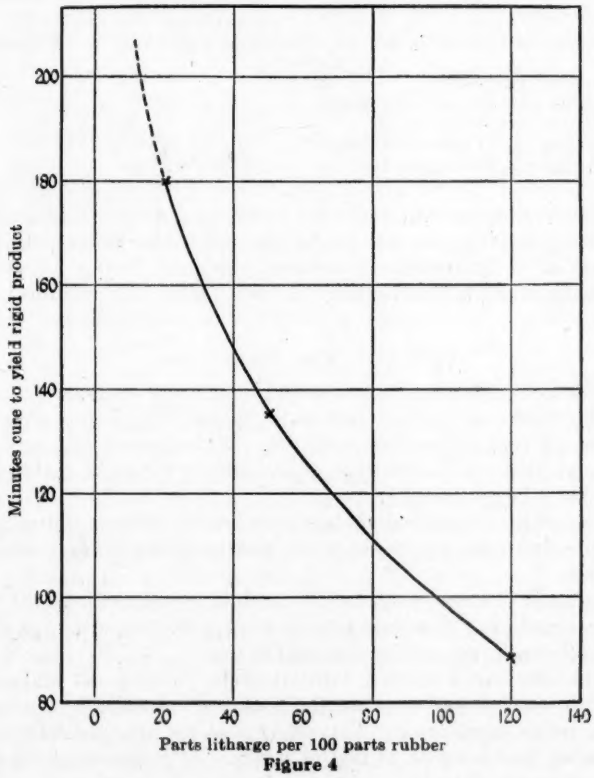

Figure 4

$1^1/_2$ hours, the samples of the second group cracked and broke "short" when bent, and were obviously nearly fully hardened.

It was concluded that a minimum quantity of 140 parts of vulcanizing agent was necessary to obtain the hard product, and trials showed that little advantage accrued from the use of larger quantities.

Analysis of the Hard Product.—Hard products were prepared by press-heating a mix consisting of smoked sheet rubber 100, *m*-dinitrobenzene 160, litharge 50, stearic acid 3, for 4 hours (A) and 5 hours (B). Each sample was filed and the dust passed through a 60-mesh screen before acetone extraction to remove free *m*-dinitrobenzene. Extraction was thought to be complete after 90 hours, so the

solvent was renewed and the flask replaced. After 120 hours, however, a further small quantity had been removed, the solvent being just tinted yellow. Extraction was then considered virtually complete. The acetone extract presented no features calling for comment.

The nitrogen contents of the original samples, of the extracted samples, and of the acetone extracts were then determined by a modification of Kjeldahl's method. The results were as follows:

	Sample A (4 Hours' Cure) Per Cent	Sample B (5 Hours' Cure) Per Cent
Acetone extract	26.3	25.1
Nitrogen content of extract	14.4	14.33
Free *m*-dinitrobenzene (% of vulcanizate)	22.7	21.6
(The above figures are probably low on account of slight loss by sublimation during drying)		
Nitrogen content of vulcanizate	8.35	8.40
Total *m*-dinitrobenzene (% of vulcanizate)	50.2	50.4
Nitrogen content of extracted sample	5.40	5.38
Combined nitrogen (% of extracted sample)	32.4	32.3
Combined nitrogen (% of vulcanizate)	24.1	24.55

From these figures it appears that about 5 parts of the vulcanizing agent were lost during processing, leaving 155 parts per 100 parts of rubber in the vulcanizate. Of this 74.2 parts of *m*-dinitrobenzene became combined during 4 hours' heating, and 75.5 parts during 5 hours' heating. Clearly, then, the reaction had reached its conclusion.

Part III. The Mechanism

The conclusions drawn from Parts I and II may first be stated.

1. When solutions of purified rubber in xylene were boiled with *m*-dinitrobenzene for long periods no reaction occurred. When heated with certain metallic oxides rubber yielded small quantities of insoluble rubber-like material. Higher oxides produced a larger quantity.

2. When solutions of purified rubber were heated with *m*-dinitrobenzene and a metallic oxide, vulcanization, as shown by gelation, occurred only after very long heating periods.

3. The addition of small quantities of fat acid greatly reduced the time necessary to produce gelling. The time now resembled that required for the gelation of technical rubber solutions without added fat acid.

4. Basic metallic oxides reacted with fat acids, yielding salt and water. The metallic salts exerted no influence on the speed of vulcanization, whereas water was found to be an accelerator. This effect was not reproducible with methyl cyclohexanone or nitrobenzene in lieu of water. Also the excess of basic oxide appeared to act as an activator.

5. In the presence of aqueous alkali and at temperatures at which vulcanization proceeds rapidly, *m*-dinitrobenzene was partially reduced. The main reduction products appeared to be azo and azoxy compounds.

6. Some products of the vulcanization of rubber in solution were identified, and their nature was similar to those mentioned in 5 above. Although all the nitrogen was accounted for, only a small part of the oxygen made available could be traced in the form of oxidation product, and it was inferred that the remainder had combined with the rubber.

7. Some nitrogen was rendered unextractable by hydrocarbon solvents, and was considered to have entered into combination with the rubber.

8. In the presence of water and a large quantity of *m*-dinitrobenzene, the vulcanization reaction proceeded to an end-point, as shown by the combined nitrogen, and formed a hard vulcanizate resembling ebonite. The water may be added on the mill or may be formed *in situ* by incorporation of a fat acid to react with part of the basic oxide in the mixture.

9. The quantity of oxide present was a factor in determining the time of heating necessary. For curing times of 2 to 3 hours at 153° C., from 20 to 100 parts (2 to 10 volumes) per 100 parts of rubber were required.

10. The minimum quantity of *m*-dinitrobenzene required to yield a hard product within four hours at 153° C. was about 140 parts per 100 parts of rubber. Of this, only about one-half entered into combination, judged by the percentage of combined nitrogen in the vulcanizate.

Discussion

The results show that the chemical changes associated with vulcanization are complex. There is no doubt that some nitrogen becomes unextractable by acetone and by hydrocarbon solvents, and may consist of nitrogen combined with the rubber, or of some insoluble nitrogen compound dispersed in the vulcanized product. It is unlikely, however, that a simple organic nitrogen compound would be insoluble in both types of solvent, and it seems reasonable to consider it as combined with the rubber.

There is also no doubt that the *m*-dinitrobenzene becomes reduced during vulcanization, and the formation of a direct additive compound with rubber as suggested by Blake is therefore unlikely. Most of the oxygen made available could not be traced in the form of oxidation products, thereby suggesting that it had combined with rubber. The reduction product appeared to be mainly dinitroazoxybenzene, rather than a nitroso compound, as suggested by Ostromislensky. The amount of oxygen which would become available from such a reduction agrees tolerably with the amount found experimentally to be missing. Without doubt, however, traces of nitroso compound and some amine were also formed.

In Part I the amount of reduction product in the xylene solution was determined by a volumetric method. As all the nitrogen was accounted for, and part of it was combined with the rubber, it follows that the portion which had combined with the rubber was in the form of reduction product and possessed a reducible residue such as the azoxy grouping. Thus, the conclusion is reached that both the oxygen and the nitrogenous residue become separately attached to the hydrocarbon chain.

The hard product which has been prepared may be assumed to be chemically saturated. If it were the oxygen analog of sulfur-cured ebonite it would have a vulcanization coefficient of about 23. This follows from the general rule that the earlier members of a group of the periodic table are less likely to form a large number of co-valent linkages, and so it may well be assumed that an oxygen atom would satisfy not more than one double bond in the hydrocarbon chain. Now the analysis of the hard product shows that it contained 24.55 per cent of combined *m*-dinitrobenzene, which is equivalent to 75.6 parts of *m*-dinitrobenzene combined with 100 parts of rubber. If this were reduced to the azoxy compound, 10.8 parts of oxygen would become available for combination with 100 parts of rubber. This quantity is almost exactly one-half the expected coefficient, and it follows that one-half of the unsaturated bonds of the rubber molecule are saturated by oxygen and the remainder by the nitrogenous residue. Thus, if the 1.5 atoms of oxygen made available per mol. of *m*-dinitrobenzene satisfy 1.5 double bonds, it

follows that the nitrogen residue also satisfies 1.5 double bonds or the whole molecule of *m*-dinitrobenzene saturates 3 double bonds. Blake (*Ind. Eng. Chem.*, **29,** 866 (1937)) considered that a mol. of this reagent saturates about 6 double bonds.

The Accessory Substances.—The presence of water seems to be highly desirable, if not essential, for the production of both soft and hard vulcanizates. Some of the best results have been obtained by the production of water *in situ*, from which it might be inferred that possibly the beneficial influence is associated with the transfer of energy liberated during the reaction between oxide and fat acid, or with one of the other secondary reactions. Such free energy would favor polymerization of the rubber hydrocarbon chains, thus bring about vulcanization rather than mere oxidation. Nevertheless, the water added as such exerts a marked influence on the rate of vulcanization. This water could not be replaced by certain organic solvents, and it therefore seems certain that water exerts a specific influence. Such action may be similar to that involved in the setting of ethylene polysulfide plastics, in which case a basic oxide is also needed.

The reduction of the vulcanizing agent can proceed only in alkaline media, and the role of the basic oxide is thus obvious. The action of water is probably associated with its hydroxyl ions. Its function apparently is to react with the basic oxide forming a hydroxide which, in the case of lead and barium, becomes ionized. Thus, in the experiments lead hydroxide did not accelerate in the absence of water.

The activating effect of the excess of oxide is not so readily explained. It probably catalyzes the reduction of the nitro compound in some manner. It is possible that unstable higher oxides may be formed temporarily, although no experimental evidence of this is available.

It is believed, then, that although the hard product obtained resembles sulfur-cured ebonite in a number of respects, it is not strictly the oxygen analog.

With regard to the monomolecular reaction found by Boggs and Blake (*Ind. Eng. Chem.*, **22,** 748 (1930)), it is now evident that their study of the kinetics of soft rubber vulcanization was based on the erroneous premise that stable pure soft vulcanizates are formed by nitro compounds. Hard products are certainly formed, and in view of the presence of fat acid and traces of moisture in all technical raw rubber, it now seems certain that their soft vulcanizates were not uncontaminated with higher vulcanizates.

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The Activating Influence of Metallic Oxides on Vulcanization in the Presence of Organic Accelerators

F. H. Cotton and J. Westhead

Department of Chemistry and Rubber Technology, Northern Polytechnic, London

Introduction

In mixes for soft vulcanized rubber, zinc oxide is almost as frequent an ingredient as sulfur, in virtue of the proved ability of this oxide to activate organic accelerators and facilitate an efficient cure. It has been observed, however, that zinc oxide retards the vulcanization of many ebonite mixes.

Little has been published regarding the activating influence of other metallic oxides on vulcanization in the presence of organic accelerators, although litharge and magnesium oxide have been recommended for use with some accelerators under certain conditions, and cadmium oxide has occasionally been stated to have activating properties, though more frequently cited as an anti-scorching agent.

Dinsmore (*Ind. Eng. Chem.*, **21**, 722 (1929)) has stated that to afford maximum activation, zinc oxide must first be converted to a rubber-soluble salt by reaction with stearic or other fat acid, either naturally present or added to the mix, except in the case of dithiocarbamates and thiuram sulfides, which appear capable of reacting directly with the oxide.

The investigation herein reported was undertaken to find whether other metallic oxides could exert a similar or superior activating influence on vulcanization in the presence of typical organic accelerators, and to determine the effect of fat acids in conjunction with such oxides.

Experimental

The earlier experiments were made employing oxides of zinc, cadmium, and mercury, magnesium, calcium, and barium, with a wide range of accelerators, including examples of the seven common chemical classes; but for systematic work with all available metallic oxides it became necessary to confine attention to two commercial accelerators. Diphenylguanidine and mercaptobenzothiazole were chosen as representative of basic and acidic compounds.

With the exception of zinc oxide, the oxides used in the investigation were all obtained from a reputable chemical source, and are believed to have been pure samples. Time did not permit the individual oxides to be analyzed, and it has not been possible to determine the particle size of the materials employed, which were all obtained in the condition of fine powders (with the exception of barium oxide, which was reduced by grinding in a mortar until it would pass through a sieve of mesh 180 to the inch).

In view of the recognized influence of fat acids in facilitating vulcanization in the presence of certain organic accelerators, it was deemed necessary to find the effect of small additions of stearic acid on the activating influence exerted on vulcanization by the range of oxides investigated. As it was further believed that the fat acids normally present in rubber might have a profound effect on the com-

bination of metallic oxide and organic accelerator, it was decided at an early stage to extend the work to cover compounds containing raw rubber from which the natu-

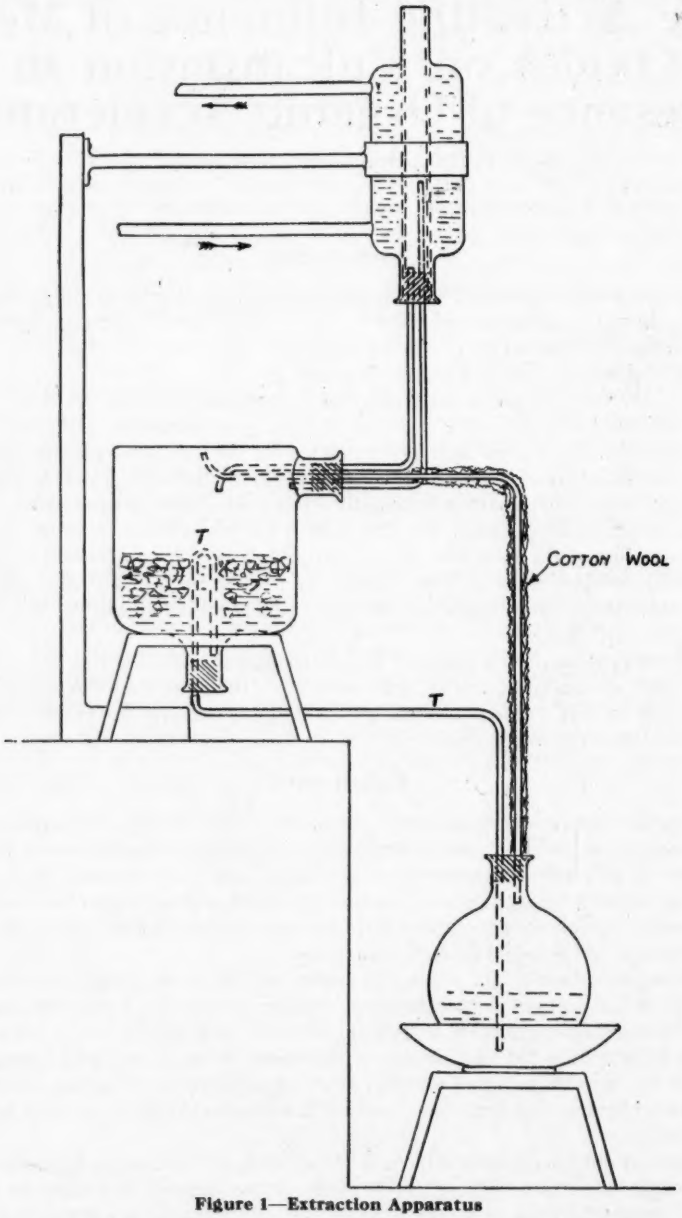


Figure 1—Extraction Apparatus

ral resinous material had been exhaustively extracted by hot acetone. Owing to the large amount of rubber required for such an extended research as was planned,

the special extraction apparatus illustrated in Fig. 1 was devised for this purpose. Five-pound batches of smoked sheet and pale crepe, respectively, were cut into small pieces and placed in a large aspirator bottle, where they were extracted by means of a continuous stream of pure acetone coming from the condenser connected, as indicated, with the round-bottomed flask serving as distillation vessel. At intervals the layer of acetone in the extraction vessel rose above the level of the syphon tube T and caused the whole of the contents to be discharged into the distillation flask.

This apparatus worked on the same principle as a Soxhlet extractor and functioned well; but difficulty was experienced in removing the extracted rubber through the neck of the bottle. A vessel with a wide stopper top would overcome this objection. In some cases, it was found more convenient to extract small quantities in the largest size of Soxhlet extractor obtainable.

The raw rubber employed throughout the investigation consisted of equal parts by weight of pale crepe and smoked sheet. In the case of acetone-extracted rubber, smoked sheet and pale crepe were extracted separately, dried in a stream of carbon dioxide, and mixed during the process of mastication. Care was taken to prevent undue access of air to extracted rubber samples, which were stored in closed desiccators both before and after vulcanization.

To obtain a rational comparison between the influence of metallic oxides employed in conjunction with different accelerators, it was decided to use such proportions of organic accelerator and sulfur as would be consistent with commercial practice. The ratios of sulfur to accelerator are given in Table I, where it will be noted that the greater the activity of the accelerator, the lower was the percentage incorporated, and the smaller the amount of sulfur added. The temperature employed for vulcanization also varied with the accelerator, as indicated in the table.

It was originally intended to employ equimolecular proportions of the range of oxides, based on 5 parts by weight of zinc oxide to 100 parts by weight of rubber in the mix. The quantities necessitated by such a stipulation in the case of antimony trioxide and arsenious oxide, red lead and bismuth trioxide appeared excessive for mere activation of acceleration. The amounts of these oxides were therefore reduced in later experiments to the proportions indicated in Table II. It was considered that, if quantities ranging from 12 to 42 per cent of oxides were incorporated, the results might be liable to criticism on the score that the loading of oxide was more than sufficient to produce accelerated vulcanization without added organic compound.

The quantities of potassium hydroxide and sodium hydroxide were also reduced to one-half their molar proportions owing to the difficulty experienced in mixing larger charges.

It was noticed that the most difficult oxide to mix on the mill was barium monoxide, which readily formed scales on the back roller and stubbornly resisted incorporation.

Throughout the work, unloaded stocks were employed, and to find the effect of varying amounts of fat acid on the activity of oxides three mixes were made with each metallic oxide, using: (1) acetone-extracted rubber; (2) raw rubber without added fatty acid; and (3) the mixture of equal parts of smoked sheet and pale crepe with an addition of 1 per cent of stearic acid.

Mastication and mixing were conducted on laboratory mills (12 in. $\times$ 6 in.), endeavoring to employ the same technic and maintain constant conditions throughout each experiment. The stock was sheeted 0.25 in. thick for vulcanization in ring molds in a platen press to give discs 3 mm. thick. The samples of each mix were

vulcanized for 10, 20, 30, 40, and 60 min., respectively; but even after the last period mentioned it was found in several cases that satisfactory vulcanization had not been achieved (*e. g.*, lead dioxide, potassium oxide, and sodium monoxide in stocks accelerated with diphenylguanidine).

Tensile strength tests were made on ring-shaped test-pieces cut from the discs and stretched on a Schopper tensile testing machine. In comparing the state of cure of vulcanized mixes, it was considered more reasonable to take the modulus at 500-per cent elongation as an indication of degree of cure rather than to rely on the ultimate tensile strength determined from a maximum of three rings.

Results

1. *Oxides of Group 2 in the Periodic Classification of the Elements.*—It was natural that attention should be directed first to the oxides of the more commonly occurring elements in that group of the periodic classification which contains zinc, the oxide of which has been universally employed for activating organic accelerators. Preliminary work was therefore done with equimolecular proportions of oxides of magnesium, calcium, and barium, zinc, cadmium, and mercury, based on 5 parts by weight of zinc oxide, with 100 parts of rubber in the mix. It was originally hoped to investigate the oxides in each group of the periodic table with a wide range of organic accelerators; but this has not yet been possible. However, in the early work with the oxides mentioned, mixes were made containing accelerators representative of the aminealdehyde condensation type, the guanidine class, dithiocarbamates, xanthates, thiuram disulfides, and mercaptobenzothiazole (see Table I).

TABLE I

ACCELERATOR AND SULFUR IN MIX

Ref. No.	Group	Typical Member Chosen	Used (%)	Sulphur (%)	Temperature of Vulcanisation (° C.)
1	Dithiocarbamates	Piperidine salt of pentamethylenedithiocarbamic acid	0.30	2.00	115
2	Xanthates	Zinc salt of ethylxanthic acid	0.30	2.00	115
3	Thiurams	Tetraethylthiuram disulfide	0.40	2.00	126
4	Aldehydeamines	Butyraldehydeamine	0.75	2.50	135
5	Guanidines	Diphenylguanidine	1.00	3.00	142
6	Thiazoles	Mercaptobenzothiazole	0.75	3.00	142
7	Ethylideneanilines	Ethylideneaniline	1.00	3.00	142

The results are shown graphically in Figs. 2 and 3, from which it may be deduced that oxides of barium, calcium, and magnesium exert insignificant activating effect on vulcanization, in the presence of all the accelerators tested. On the other hand, it was surprising to find that cadmium oxide was superior in activating effect to zinc oxide in normal mixes using isopropyl xanthate, tetraethylthiuram disulfide, mercaptobenzothiazole, and ethylideneaniline. When employed in a mix utilizing acetone-extracted rubber, cadmium oxide also proved superior to zinc oxide with all accelerators tested, other than diphenylguanidine. It should be noted that in this series of experiments no additional stearic acid was added.

It may be observed that, using mercaptobenzothiazole as accelerator, mercuric oxide not only gave greater activation than zinc oxide, but was even superior to cadmium oxide. It was astonishing to find that this unexpected activity of mercuric oxide was more marked when using extracted rubber in the mix incorporating

FIG. 2.

TIME OF CURE — 30 MINUTES

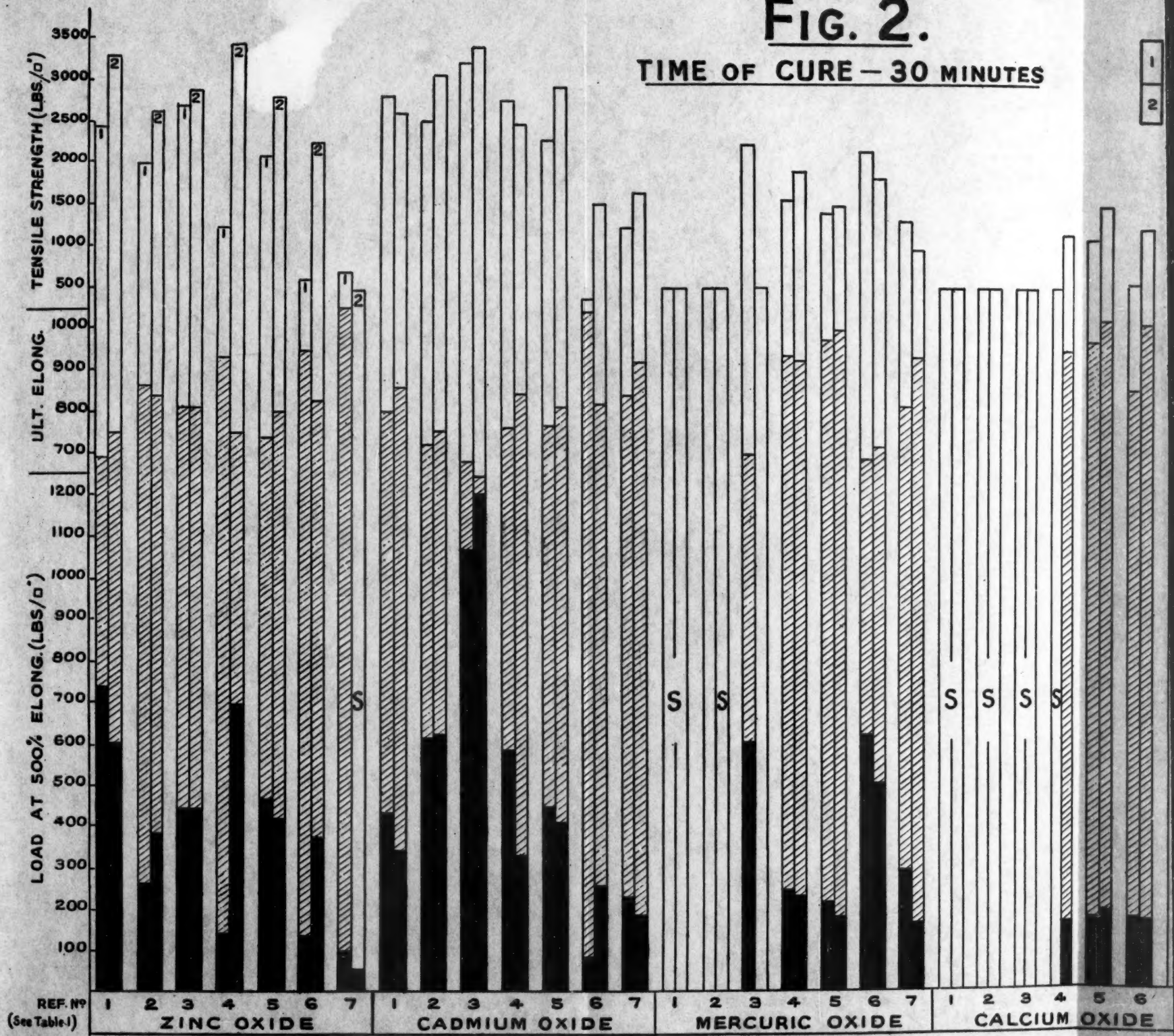
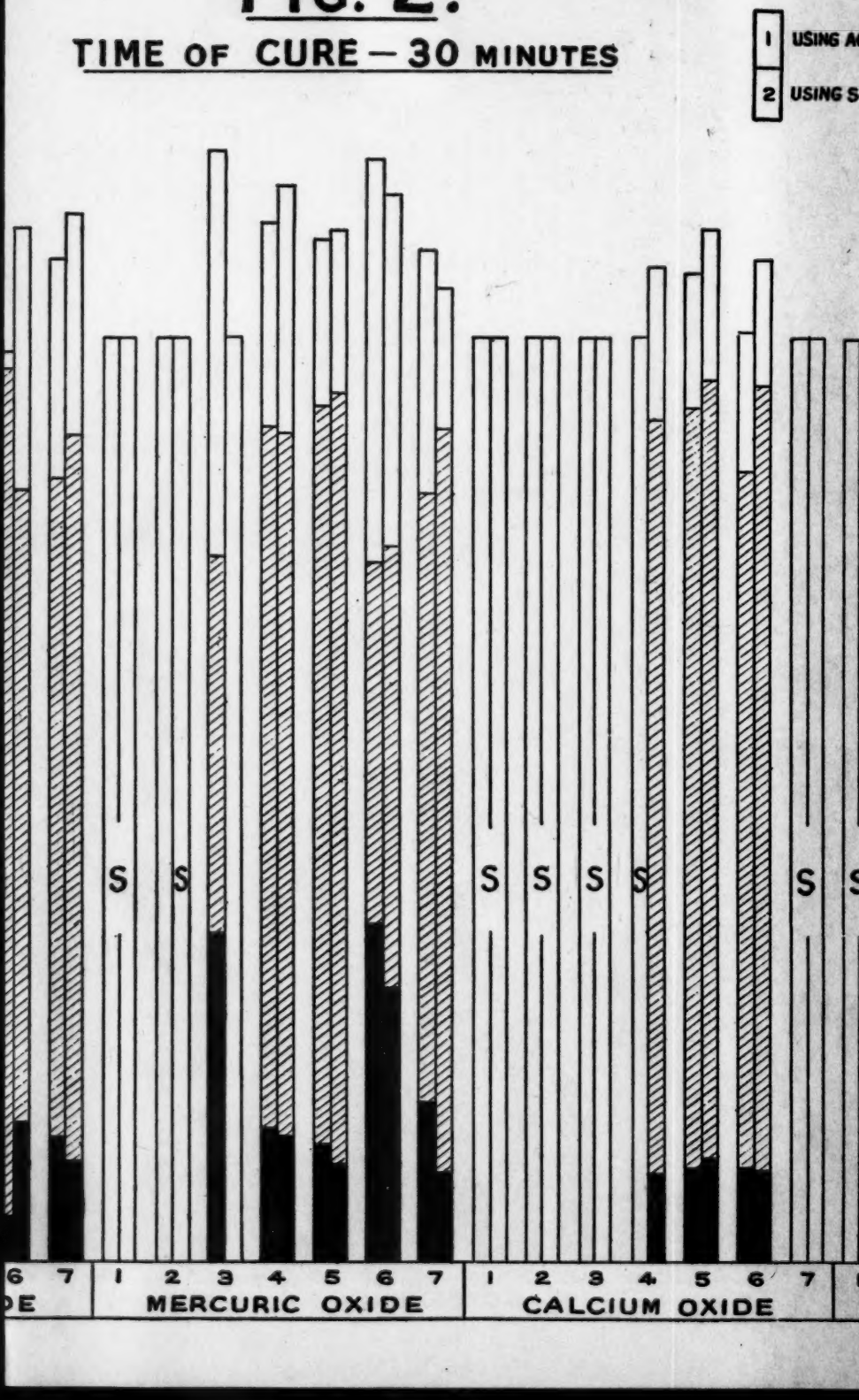
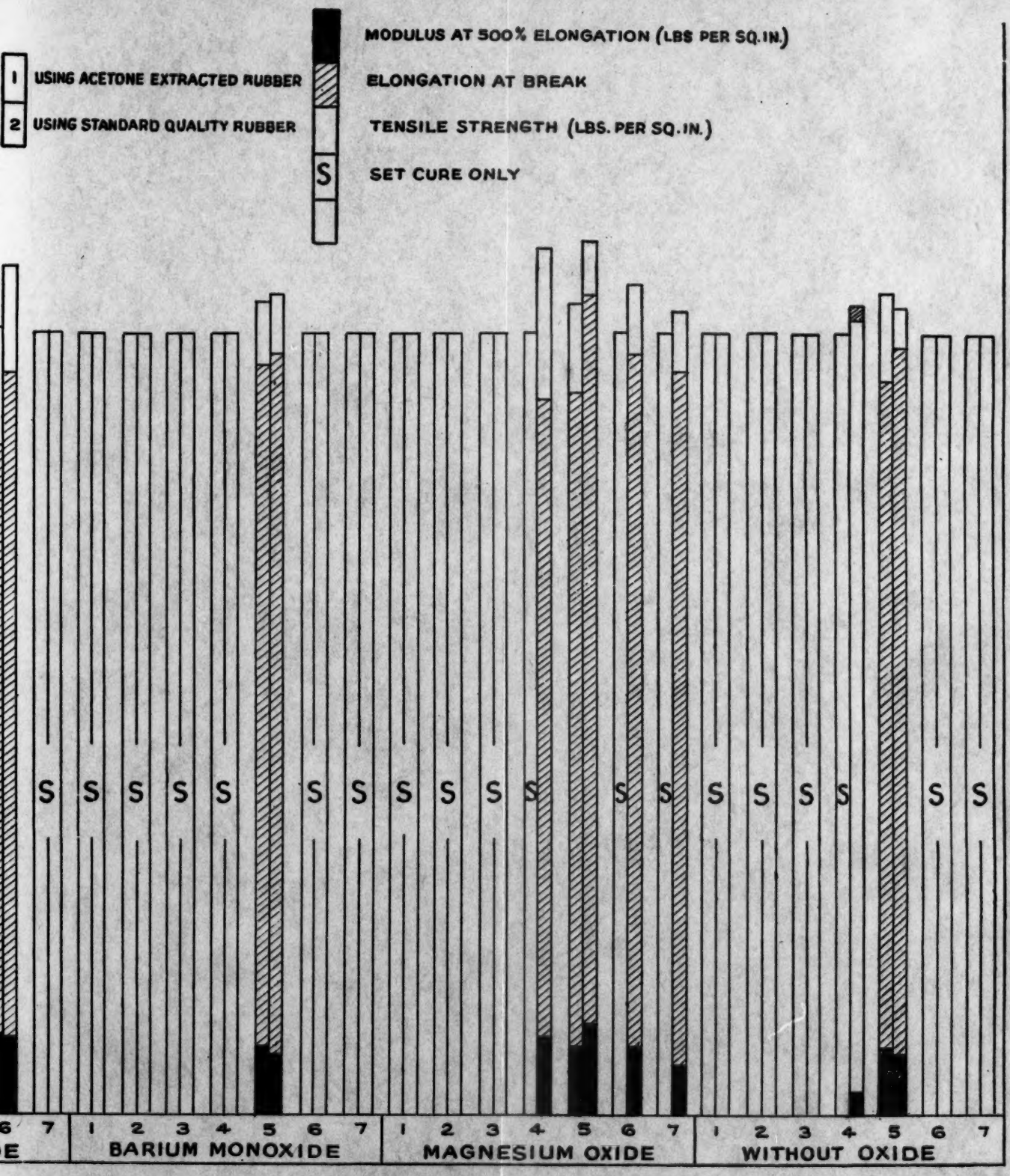
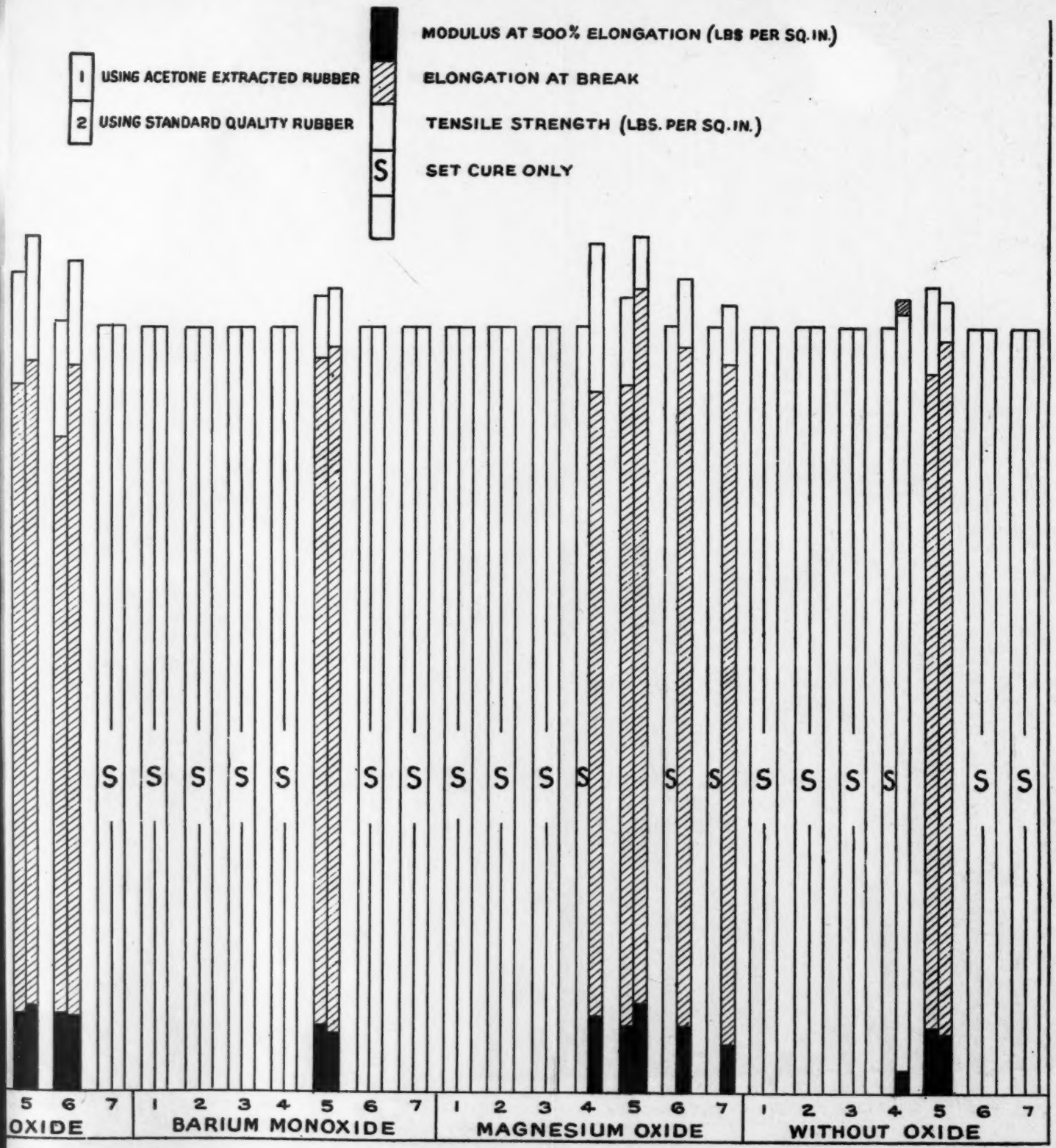


FIG. 2.

TIME OF CURE — 30 MINUTES




MODULUS AT 500% ELONGATION (LBS PER SQ.IN.)
ELONGATION AT BREAK
TENSILE STRENGTH (LBS. PER SQ.IN.)
SET CURE ONLY
1 USING ACETONE EXTRACTED RUBBER
2 USING STANDARD QUALITY RUBBER
S
6 7
E
1 2 3 4 5 6 7
BARIUM MONOXIDE
1 2 3 4 5 6 7
MAGNESIUM OXIDE
1 2 3 4 5 6 7
WITHOUT OXIDE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5 6 7 OXIDE
1 2 3 4 5 6 7 BARIUM MONOXIDE
1 2 3 4 5 6 7 MAGNESIUM OXIDE
1 2 3 4 5 6 7 WITHOUT OXIDE

mercaptobenzothiazole. Mercuric oxide also proved superior to zinc oxide when using tetraethylthiuram disulfide in an extracted rubber mix.

With the more readily obtainable oxides of the metals in Group 2 of the periodic classification, it thus appears that there is a general tendency for increased activation of the mercaptan type of acid accelerator as one passes from zinc to mercury in ascending atomic weight in Sub-Group B. With basic accelerators the general trend was in the reverse direction, that is, decreased activation as one passed from zinc to mercury. However, there were discrepancies in the case of cadmium oxide and mercuric oxide when employed with extracted rubber.

A notable feature of these earlier experiments was the surprising lack of activating power exhibited by calcined magnesia, barium monoxide, and calcium oxide.

2. *The Influence of a Range of Oxides in the Presence of Diphenylguanidine and Mercaptobenzothiazole.*—In view of the limited time available for the research, the range of oxides investigated during the later stages of the work was only employed in mixings containing a typical basic and acidic accelerator, respectively: namely, diphenylguanidine and mercaptobenzothiazole. The sulfur-accelerator ratios were as indicated in Table I and the percentages of oxide incorporated are given in Table II. The activating influence of twenty-four oxides on vulcanization in the presence of diphenylguanidine and mercaptobenzothiazole is demonstrated in the series of graphs (Figs. 4 to 10), showing the rigidity at 500-per cent elongation. In each case experiments were made using extracted rubber (A), ordinary rubber (B), and a mix including 1 per cent of additional stearic acid (C). Tables III to X summarize the results of the moduli, tensile strength, and elongation tests on vulcanized samples containing oxides which gave results equal or superior to those with zinc oxide.

TABLE II

Oxide		Molecular Weight	Molar Proportion	Parts per 100 of Rubber
Zinc oxide	ZnO	81.37	5.00	5.00
Aluminum oxide	Al_2O_3	102.00	6.30	6.30
Antimony trioxide	Sb_2O_3	288.40	17.70	8.85
Arsenious oxide	As_2O_3	197.92	12.20	6.10
Bismuth trioxide	Bi_2O_3	466.00	28.80	14.40
Barium monoxide	BaO	153.37	9.40	9.40
Calcium oxide	CaO	56.07	3.40	3.40
Chromium sesquioxide	Cr_2O_3	152.00	9.40	9.40
Cupric oxide	CuO	79.57	4.90	4.90
Cuprous oxide	Cu_2O	143.14	8.80	8.80
Cadmium oxide	CdO	128.40	7.90	7.90
Ferric oxide	Fe_2O_3	159.68	9.90	9.90
Lead monoxide (litharge)	PbO	223.20	13.80	13.80
Lead dioxide	PbO_2	239.20	14.80	14.80
Red lead	PbO_4	685.60	42.40	14.10
Mercuric oxide	HgO	216.60	13.40	13.40
Magnesium oxide	MgO	40.32	2.50	2.50
Potassium oxide (as KOH)	K_2O	94.20	6.80	3.40
Sodium monoxide (as NaOH)	Na_2O	62.00	5.00	2.50
Silica	SiO_2	60.10	3.70	3.70
Stannic oxide	SnO_2	150.70	9.30	9.30
Stannous oxide	SnO	134.70	8.30	8.30
Strontium oxide	SrO	103.63	6.40	6.40
Titanium dioxide	TiO_2	80.10	4.90	4.90

The feature of the results obtained with diphenylguanidine mixes is the marked tendency for increased activation as the fatty acid content of the rubber decreases, which is a most unexpected result. Nearly all oxides tested gave the highest m du-

lus when incorporated with a mix made with extracted rubber. The only exceptions were magnesium oxide and calcium oxide, though in the latter case lower results were only obtained with extracted rubber during the early stages of vulcanization. On the other hand, in mixes containing mercaptobenzothiazole, the tendency was for the oxides to exhibit a greater activating influence with increase in the fat

TABLE III

WITHOUT OXIDE

	Diphenylguanidine				Mercaptobenzothiazole			
	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation
A	10	99	711	1155	..	..	...	...
	20	128	909	1065	..	..	...	...
	30	152	956	1000	..	..	...	...
	40	172	1185	995	40	70	255	1080
	60	192	1248	970	60	94	499	1140
B	10	77	323	1125	..	..	...	...
	20	110	619	1125	..	..	...	...
	30	135	797	1070	30	..	200	1165NB
	40	145	988	1070	40	38	292	1165NB
	60	166	1177	1060	60	58	529	1165NB
C	10		Set		..	..	...	...
	20	71	381	1165NB[a]	..	..	...	...
	30	103	671	1165NB	30	..	129	1165NB
	40	116	890	1125	40	..	176	1165NB
	60	125	898	1100	60	39	329	1165NB

[a] NB—No break.

TABLE IV

ZINC OXIDE

	Diphenylguanidine				Mercaptobenzothiazole			
	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation
A	10	243	1535	833	10	81	527	1015
	20	314	1934	770	20	121	565	975
	30	465	2086	742	30	135	587	950
	40	561	2280	728	40	144	656	910
	60	680	2170	677	60	153	486	845
B	10	219	2167	918	10	294	1962	845
	20	320	2293	880	20	349	2149	830
	30	414	2806	798	30	368	2275	825
	40	527	2952	765	40	374	2219	835
	60	595	3137	758	60	356	1888	825
C	10	146	1192	1060	10	293	2125	845
	20	220	1905	965	20	380	2333	810
	30	301	2243	870	30	424	2333	800
	40	356	2301	840	40	436	2257	785
	60	443	2271	770	60	405	2232	813

acid content of the rubber; the only marked exception being the case of mercuric oxide. In several instances the fatty acid in excess of that naturally present in the rubber appeared to act merely as a softener, causing a slight decrease in the modulus.

Although the development of modulus was retarded by an increase in the fat acid content of a diphenylguanidine mix, it was frequently observed that the ten-

FIG. 3.

TIME OF CURE 60 MINUTES

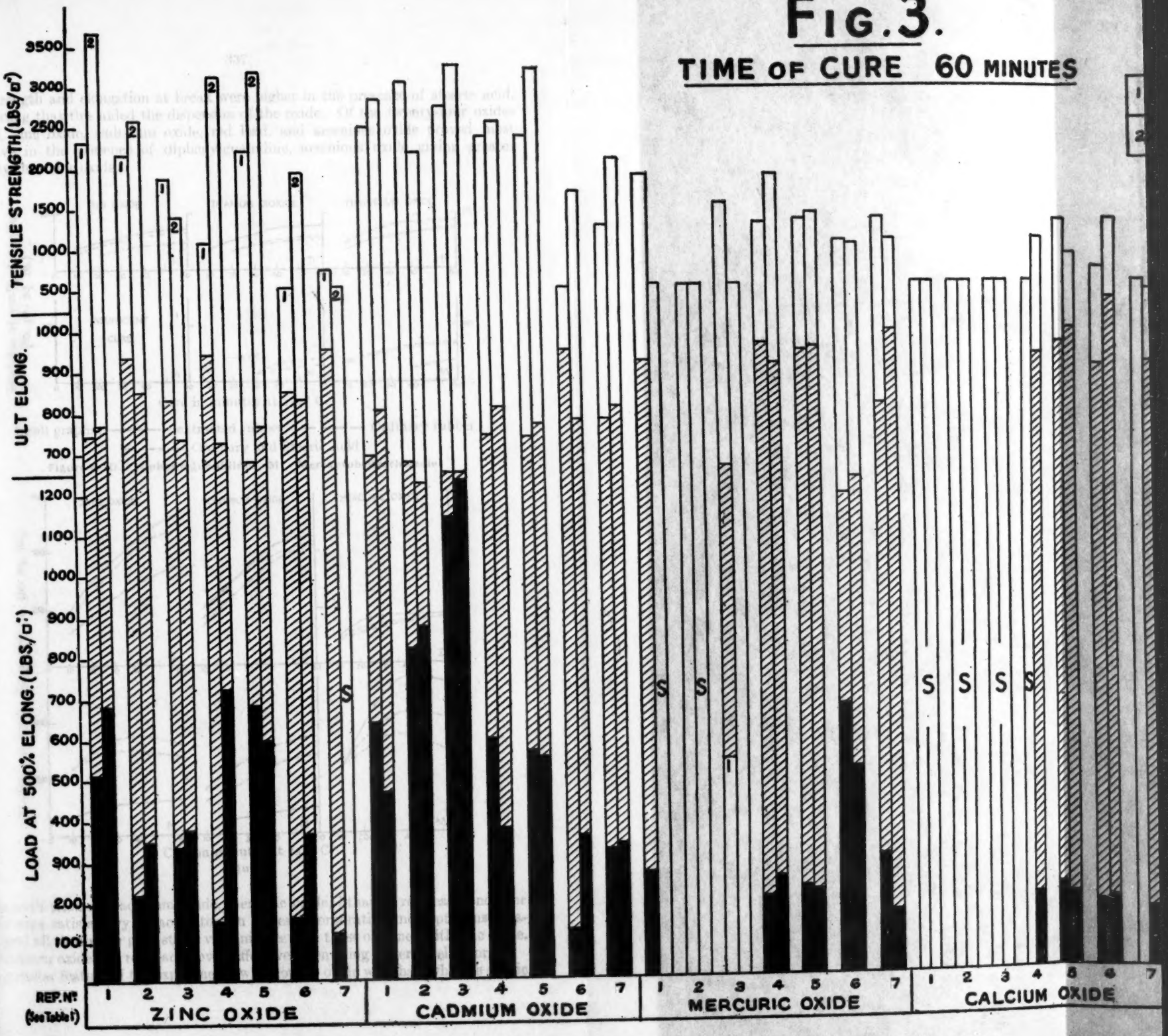
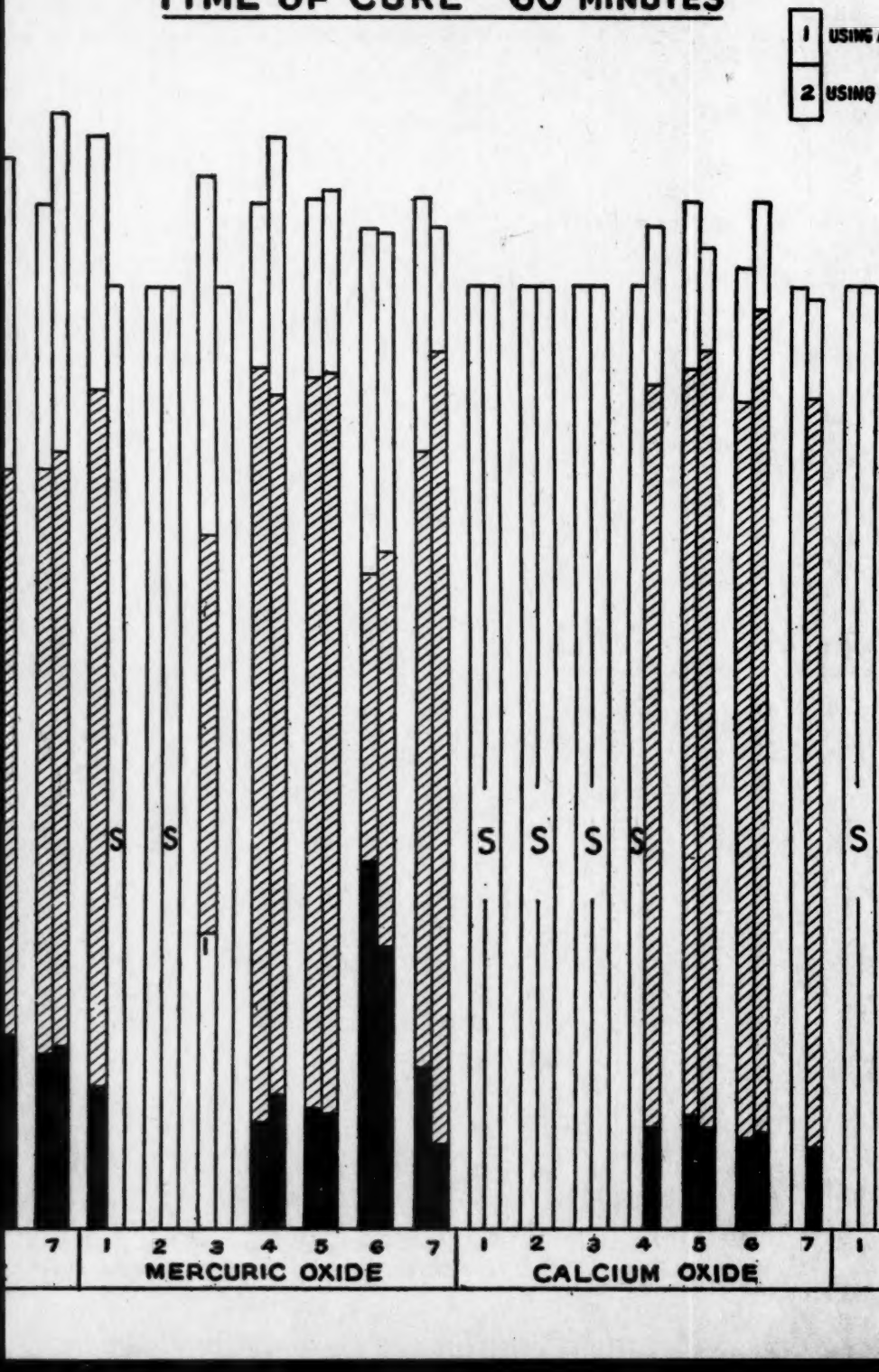
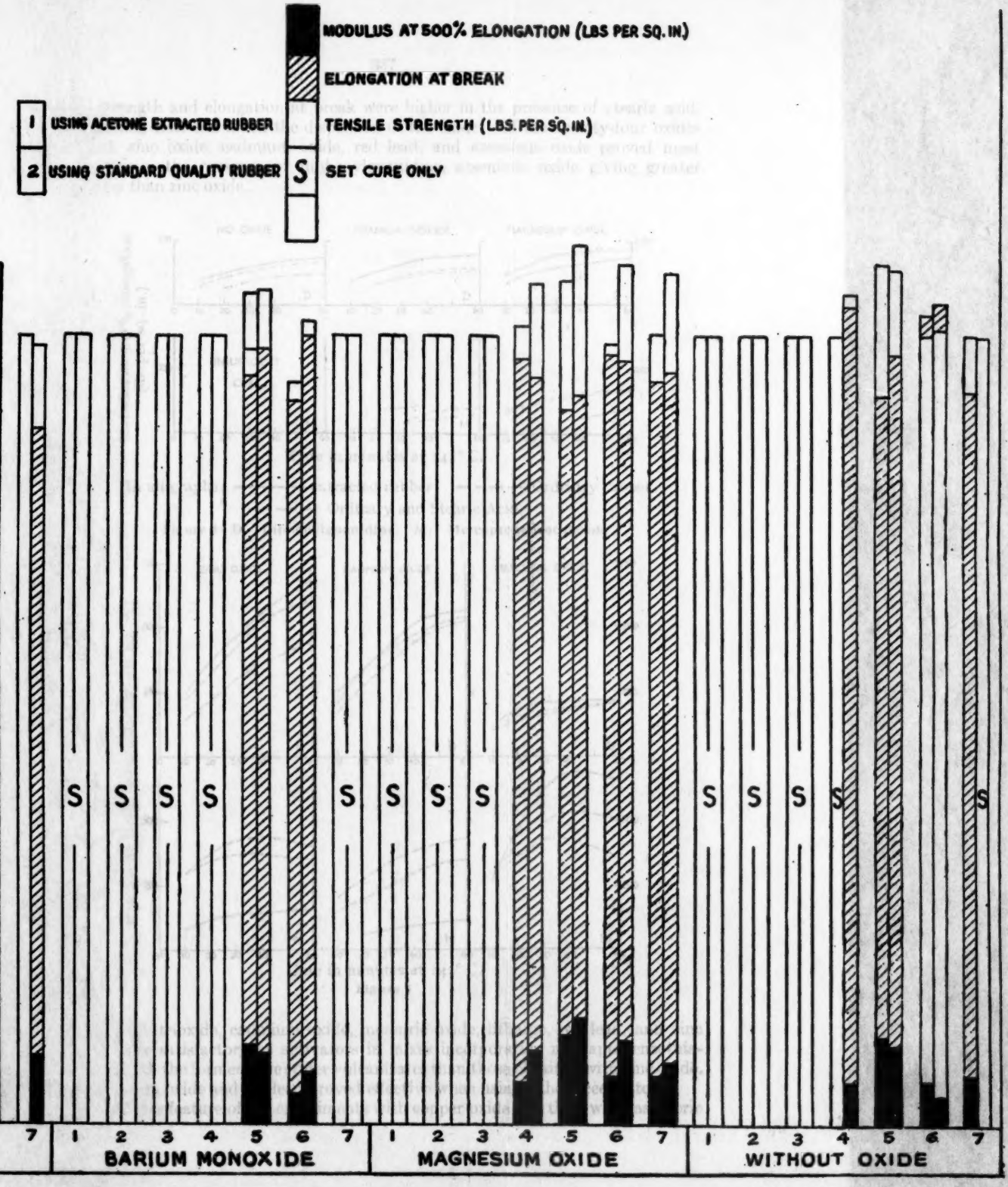


FIG. 3.

TIME OF CURE 60 MINUTES

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ELONGATION AT BREAK
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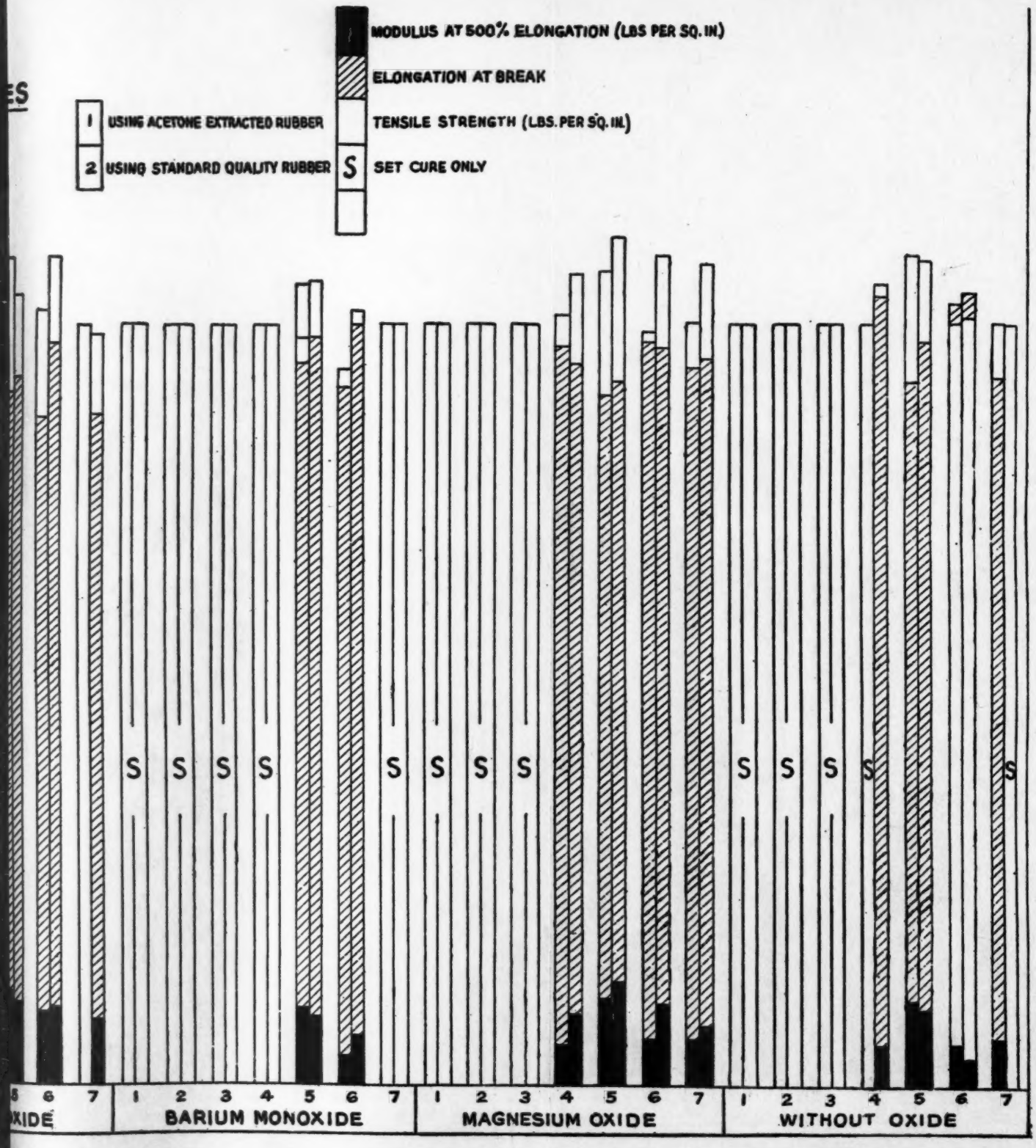
S S S S S S S S S S S S S S
7 1 2 3 4 5 6 7 1 2 3 4 5 6 7 1 2 3 4 5 6 7
BARIUM MONOXIDE
MAGNESIUM OXIDE
WITHOUT OXIDE


MODULUS AT 500% ELONGATION (LBS PER SQ. IN.)
ELONGATION AT BREAK
TENSILE STRENGTH (LBS. PER SQ. IN.)
S SET CURE ONLY
1 USING ACETONE EXTRACTED RUBBER
2 USING STANDARD QUALITY RUBBER
S S S S S S S S S S S S S S
5 6 7 1 2 3 4 5 6 7 1 2 3 4 5 6 7 1 2 3 4 5 6 7
XIDE
BARIUM MONOXIDE
MAGNESIUM OXIDE
WITHOUT OXIDE

sile strength and elongation at break were higher in the presence of stearic acid, suggesting that this aided the dispersion of the oxide. Of the twenty-four oxides tested, zinc oxide, cadmium oxide, red lead, and arsenious oxide proved most effective in the presence of diphenylguanidine, arsenious oxide giving greater rigidity than zinc oxide.

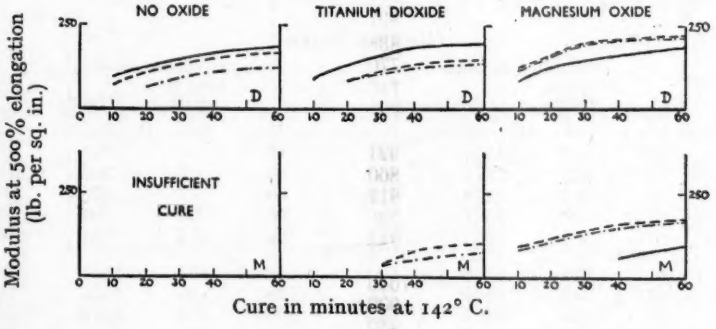


Figure 4—D. Diphenylguanidine. M. Mercaptobenzothiazole

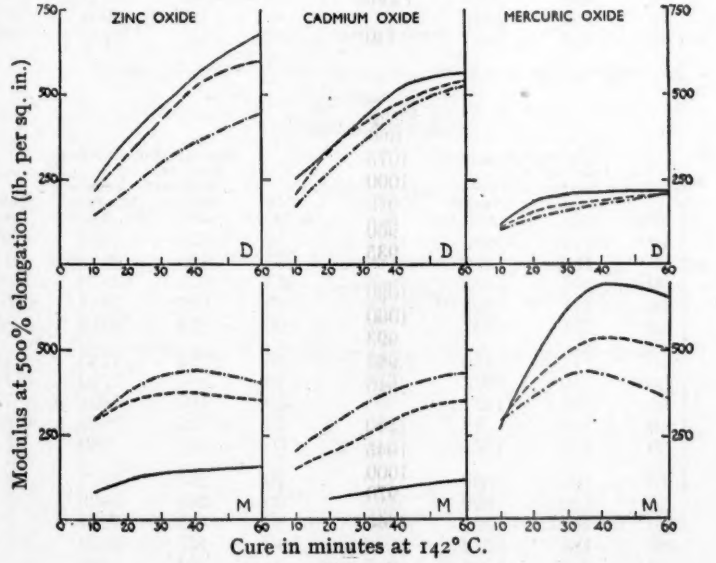


Figure 5

Bismuth trioxide, cadmium oxide, mercuric oxide, litharge, red lead, and zinc oxide were satisfactory as activators in mixes incorporating mercaptobenzothiazole, and all the former gave stiffer vulcanizates than those obtained with zinc oxide. Cadmium oxide and red lead proved effective when using either accelerator.

A peculiar feature of the experiments with copper oxide was that, whereas cupric

oxide showed distinct activating properties, an equimolecular proportion of cuprous oxide caused such rapid deterioration during and subsequent to cure, that it was impossible to complete the physical tests. The only reference found to previous work on the deteriorating effect of cupric and cuprous oxide was by Ditmar (*J. Soc. Chem. Ind.*, **35**, 643 (1916)), who reported that cupric oxide in a non-ac-

TABLE V

CADMIUM OXIDE

	Diphenylguanidine				Mercaptobenzothiazole			
	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq.In.)	Elongation
A	10	255	1864	897	10		Set	
	20	343	2271	838	20	65	305	1080
	30	442	2244	770	30	77	338	1040
	40	520	2327	740	40	98	404	990
	60	564	2335	725	60	114	481	940
B	10	208	1778	921	10	152	1352	960
	20	343	2917	860	20	195	1425	925
	30	418	2904	812	30	252	1479	820
	40	478	3068	785	40	303	1784	810
	60	546	3130	754	60	350	1627	765
C	10	174	1716	1040	10	205	1301	855
	20	275	2121	900	20	273	1956	830
	30	366	2600	850	30	344	2074	800
	40	449	2607	800	40	380	2003	775
	60	537	2645	750	60	431	2113	765

TABLE VI

MERCURIC OXIDE

	Diphenylguanidine				Mercaptobenzothiazole			
	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq.In.)	Elongation
A	10	121	940	1075	10	270	1864	855
	20	190	1416	1000	20	460	2048	740
	30	207	1428	970	30	621	2126	685
	40	211	1398	960	40	692	1884	655
	60	211	1302	935	60	658	1019	580
B	10	112	756	1090	10	292	1755	817
	20	159	1312	1060	20	407	1799	755
	30	175	1477	993	30	493	1801	713
	40	193	1518	983	40	536	1649	675
	60	208	1374	940	60	501	980	617
C	10	106	686	1110	10	290	1671	820
	20	139	820	1045	20	368	1933	794
	30	163	1081	1000	30	427	1944	750
	40	185	1312	970	40	427	1659	738
	60	213	1305	935	60	362	1639	790

celerated mix caused more rapid deterioration than cuprous oxide, the latter acting as an accelerator.

3. *Use of Arsenious Oxide, Red Lead, and Litharge as Accelerators.*—In view of the fact that several of the oxides tested gave mixes which vulcanized more rapidly than the control containing zinc oxide, it became necessary to determine whether

the effect of these oxides was really an activation of the organic accelerator or whether, in the quantities employed, the oxides themselves were functioning as accelerators. For this purpose, arsenious oxide (which gave the best results in mixes incorporating diphenylguanidine), litharge, and red lead (which proved superior in

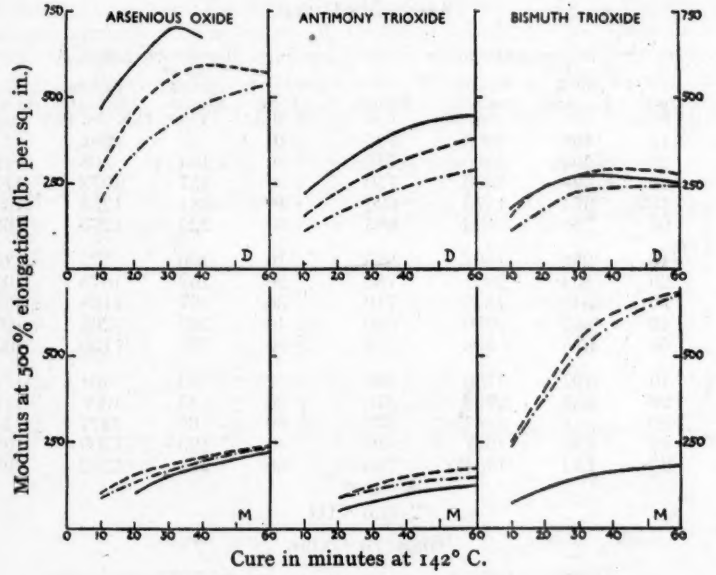


Figure 6

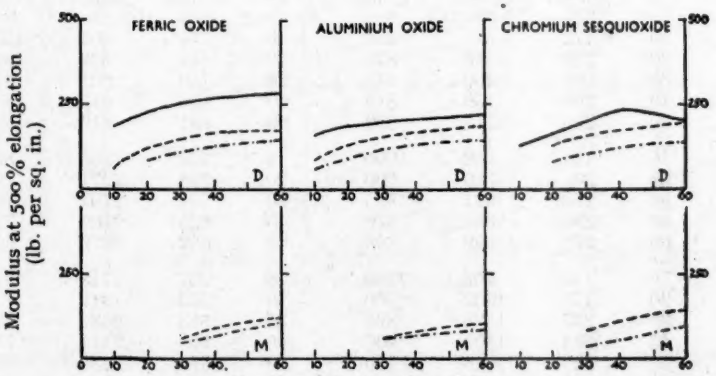


Figure 7

mercaptobenzothiazole stocks) were tested in mixes of the same composition as used for the previous work, with the exception that the organic accelerator was omitted from the mix.

The results are given graphically in Fig. 11. If these be compared with the corresponding graphs referring to the influence of the oxides in the accelerated mixes, it

will be observed that the rate of vulcanization and the ultimate moduli obtained are much inferior, thus indicating that the effect of these oxides in mixes containing organic accelerators may legitimately be ascribed to activation.

TABLE VII

ARSENIOUS OXIDE

	Diphenylguanidine				Mercaptobenzothiazole			
	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation
A	10	468	2295	785	10		Set	
	20	593	2395	775	20	104	565	1150
	30	699	2489	750	30	157	1073	1125
	40	674	1173	620	40	181	1253	1090
	60	...	433	395	60	225	1275	1050
B	10	288	1507	895	10	106	575	1100
	20	464	2051	780	20	162	1075	1090
	30	546	1529	710	30	187	1198	1075
	40	592	1050	630	40	205	1265	1050
	60	575	598	518	60	233	1150	1025
C	10	197	1706	990	10	89	461	1125
	20	335	2077	870	20	133	1005	1110
	30	418	2164	835	30	162	1227	1100
	40	476	2027	810	40	199	1409	1085
	60	542	1454	700	60	228	1382	1055

TABLE VIII

BISMUTH OXIDE

	Diphenylguanidine				Mercaptobenzothiazole			
	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation
A	10	172	981	950	10	76	406	1005
	20	236	1248	875	20	117	528	935
	30	269	1260	845	30	150	661	915
	40	269	1159	815	40	159	687	890
	60	255	1217	850	60	181	819	890
B	10	151	950	1000	10	252	1698	860
	20	245	1580	900	20	398	2271	795
	30	270	1611	885	30	551	2707	760
	40	286	1664	870	40	625	2600	720
	60	279	1599	895	60	682	2379	695
C	10	110	768	1110	10	237	1718	875
	20	178	1332	960	20	372	1917	775
	30	237	1335	890	30	513	2530	750
	40	244	1403	900	40	595	2414	715
	60	249	1376	910	60	679	2238	680

Discussion

Vulcanization is believed to consist in addition of sulfur to rubber while the latter is being disaggregated by heat. The more rapidly sulfur is added, the less chance of reversion and the greater the strength of the resulting product for a given percentage of combined sulfur. It seems that normal molecules of sulfur cannot add rapidly to the double bonds of the rubber molecule; the sulfur must first be

transformed to a more active or atomic form, and thus the rate of combination depends on the speed of formation of active sulfur.

The favorable action of accelerators, although not strictly catalytic, may be explained by assuming that in the presence of an accelerator, active sulfur is formed more rapidly. In view of the large number of organic compounds which function satisfactorily as accelerators, it is not surprising that no single mechanism has been found to account for the action at all. Scott and Bedford (*Ind. Eng. Chem.*, **12**, 31 (1920); **13**, 125 (1921)) explained many types of accelerators, chiefly organic bases, by assuming the formation of intermediate polysulfides as the source of active sulfur. The base was thought to combine with hydrogen sulfide produced by the ac-

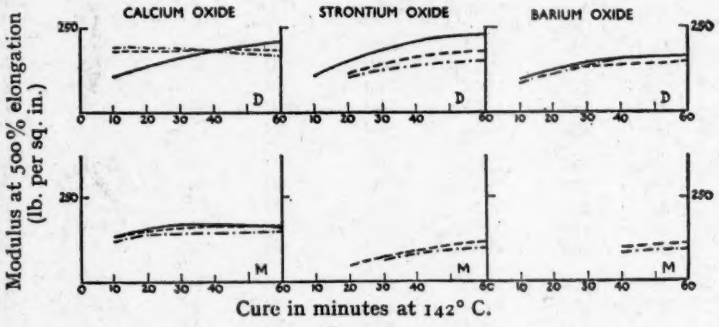


Figure 8

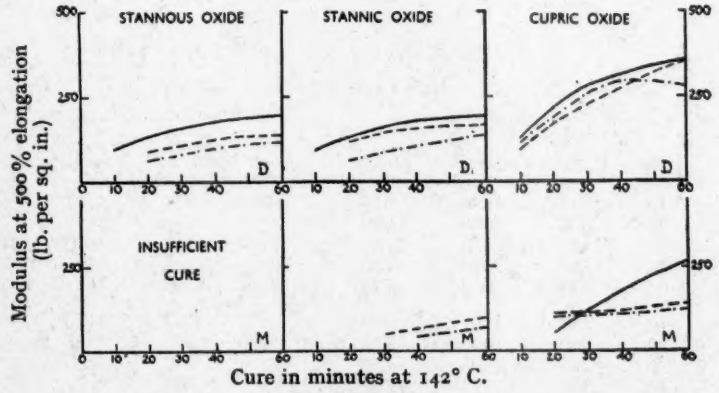


Figure 9

tion of sulfur on the protein and resins present in the rubber, forming ammonium sulfide derivatives. These addition products may react with more sulfur, forming polysulfides, which are unstable and liberate sulfur in an active state.

$$R - NH_2 + H_2S \rightarrow R - \underset{\underset{SH}{|}}{\overset{\overset{H}{|}}{N}}H_2 + S_x \rightarrow R - \underset{\underset{(S)_x}{\|}}{\overset{\overset{H}{|}}{N}}H_2 \rightarrow R - \underset{\underset{SH}{|}}{\overset{\overset{H}{|}}{N}}H_2 + xS \text{ (active)}$$

Compounds in this class have therefore been termed "hydrogen sulfide–polysulfide" accelerators. The theory, however, fails to account for the marked increase in activity of certain members of the group (such as aldehydeamines, hexamethylenetetramine, and disubstituted guanidines) in the presence of a basic oxide. The disubstituted guanidines, however, also fall into the second class known as

TABLE IX

LITHARGE

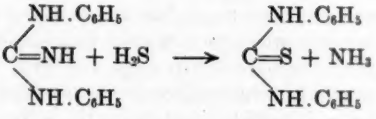
	Diphenylguanidine				Mercaptobenzothiazole			
	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation
A	10	194	1133	900	10	255	1459	835
	20	310	1272	810	20	454	2182	765
	30	361	1344	760	30	595	2549	740
	40	386	1395	750	40	688	2650	725
	60	356	1533	800	60	735	2615	708
B	10	196	1162	905	10	362	2543	830
	20	287	1858	870	20	498	2951	790
	30	368	2121	825	30	599	2738	737
	40	424	2102	775	40	629	2691	725
	60	350	1888	822	60	635	2715	730
C	10	178	1349	970	10	362	2390	828
	20	250	1724	875	20	484	2892	796
	30	316	2064	845	30	580	2756	755
	40	368	2078	810	40	583	2648	745
	60	344	1934	820	60	583	2553	740

TABLE X

RED LEAD, Pb_3O_4

	Diphenylguanidine				Mercaptobenzothiazole			
	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation	Cure (in Min.)	Load at 500% Elongation	Tensile Strength (Lb./Sq. In.)	Elongation
A	10	213	1636	915	10	228	1573	880
	20	356	2009	820	20	455	2414	780
	30	441	2150	785	30	653	2460	710
	40	536	2070	730	40	828	2881	700
	60	539	2013	720	60	1006	3114	680
B	10	190	1297	950	10	407	2472	800
	20	300	1469	810	20	562	2937	755
	30	368	1695	775	30	756	3223	718
	40	456	1714	760	40	860	3270	700
	60	586	2379	735	60	1027	3161	669
C	10	199	1435	940	10	415	2560	790
	20	277	1892	870	20	606	2750	735
	30	350	2159	820	30	769	2861	700
	40	435	2351	780	40	839	3008	670
	60	550	2595	745	60	915	3184	670

"carbosulfhydryl polysulfide accelerators," characterized by the presence of the ≡C—SH group or the ability to form this group under the conditions of vulcanization. Bedford and Scott assumed that diphenylguanidine reacts with hydrogen sulfide, forming ammonia and thiocarbanilide.



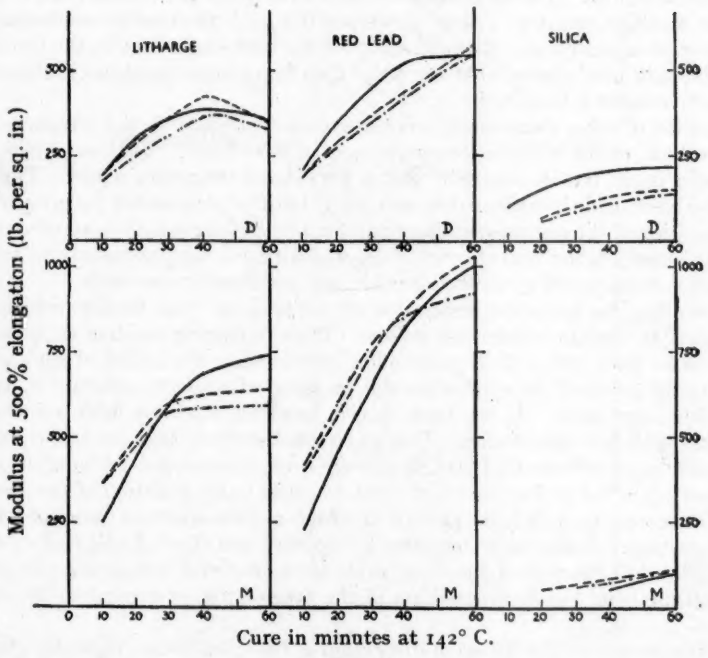


Figure 10

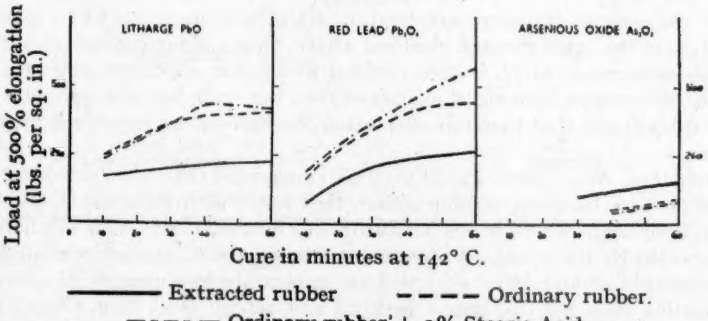
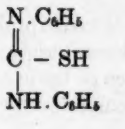

LITHARGE PbO
RED LEAD Pb3O4
ARSENIOUS OXIDE As2O3
Load at 500% elongation (lbs. per sq. in.)
Cure in minutes at 142° C.
Extracted rubber
Ordinary rubber.
Ordinary rubber + 1% Stearic Acid

Figure 11—Accelerating Effect of Oxide

The thiocarbanilide assumed thus formed is known to react with zinc oxide, and has been thought to exist in the tautomeric form:



Two theories have been advanced to explain the activity of accelerators in this latter group, but both involve interaction with a basic oxide such as zinc oxide. According to Bruni, dithiocarbamates form salts with zinc oxide, and then react with sulfur to give the disulfide, which decomposes into the monosulfide and liberates active sulfur. The monosulfide reacts with more uncombined sulfur to reform the disulfide, and the cycle of decomposition and reformation continues until vulcanization is complete. Bedford accepted the first stage, that is, the formation of the zinc salt, but believed that the latter then forms an unstable polysulfide from which active sulfur is liberated.

The action of these compounds is not assumed dependent on the presence of hydrogen sulfide, or the non-rubber components of the rubber. Further, it is not the accelerator itself, but its zinc salt, that is considered the active agent. The need for excess basic oxide is explained by assuming that the latter either (*a*) prevents the decomposition of the organo-metallic compound by hydrogen sulfide, or other acidic products formed in the mixture; or (if decomposition is not prevented) (*b*) the metallic salt is regenerated by the excess oxide, and acceleration proceeds.

The results of the present investigation are not in accord with the theories hitherto formulated to explain accelerator action. Thus diphenylguanidine could not be classed as a "hydrogen sulfide–polysulfide" accelerator, the action of such a compound being assumed dependent on the presence of resinous substances, largely comprising fatty acids. It has been shown, however, that any fatty acid present in the mix retards vulcanization. It is apparent, therefore, that the acid content of crude rubber and rubber stock is of paramount importance in determining the physical properties of the vulcanizate but is not essential to the function of the accelerator. There may be a definite acidity at which each accelerator functions to the best advantage. It has been suggested by Bedford and Gray (*India Rubber J.*, **64**, 604 (1922)) that the role of the basic oxide is to neutralize the acidic substances, either arising from the decomposition of the accelerator, or present in the rubber resins.

The importance of the degree of dispersion of basic oxides is frequently stressed. Martin and Davey (*J. Soc. Chem. Ind.*, **44**, 317 (1925)) have stated that fat acids increase the activity of organic accelerators in the presence of oxides by increasing the surface of the oxide through chemical action, thus making it react more readily with the accelerator, which is then enabled to develop maximum activity. The results of the present investigation suggest that the oxide behaves normally in extracted rubber, and that therefore dispersion through the agency of fat acid is not essential.

Whitby (*Ind. Eng. Chem.*, **15**, 1008 (1923)) suggested that when accelerators are bases or produce bases on decomposition, they form, with the acids of the rubber resin, salts or soaps which act as activators of vulcanization. This mechanism is not supported by the results of the present writers, which suggest combination of diphenylguanidine and fatty acid to form a stearate less capable of promoting vulcanization than the free base. Bedford and Sebrell (*Ind. Eng. Chem.*, **14**, 25 (1922)) claimed that diphenylguanidine forms an addition product with hydrogen sulfide, resulting from action of sulfur on resins present in the rubber. If such be the case, this compound must retard rather than accelerate vulcanization, as suggested, because it has emerged that diphenylguanidine is superior in a resin-free rubber mix.

The observed relative inactivity of mercaptobenzothiazole in the absence of basic oxides accords with the accepted characteristics of "carbosulfhydryl" accelerators. It was remarked that in the absence of basic oxide a fatty acid acts as a softener, and even retards vulcanization of a mercaptobenzothiazole stock.

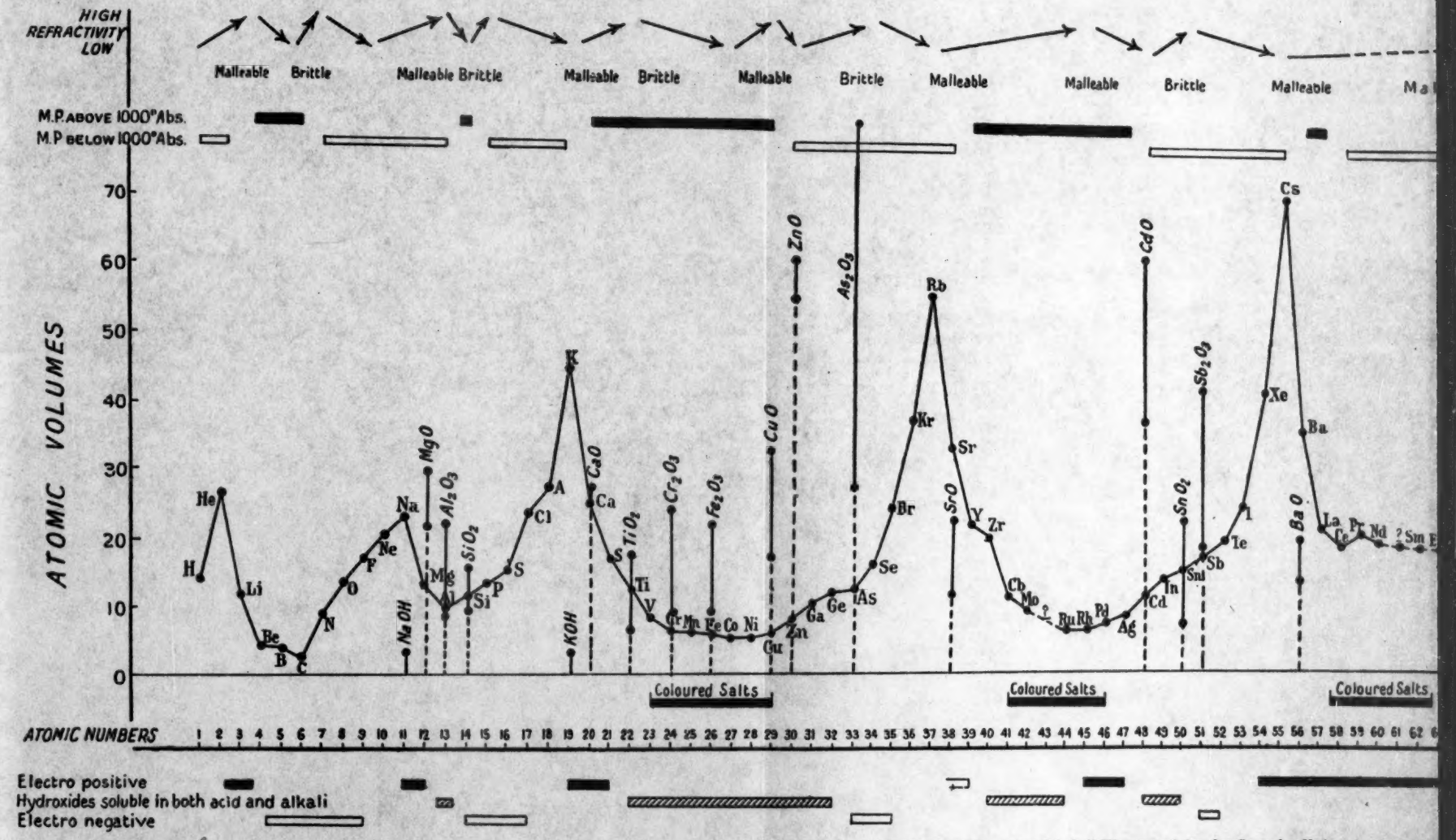
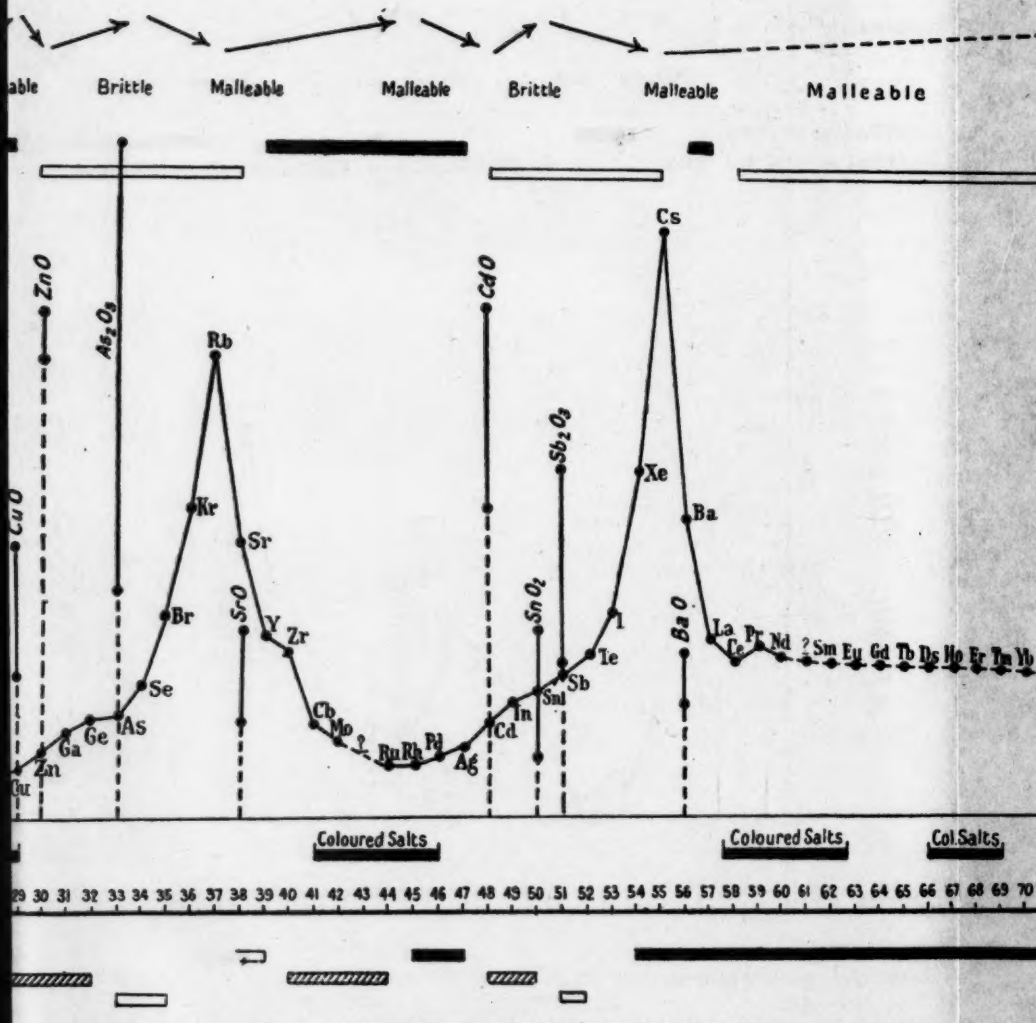
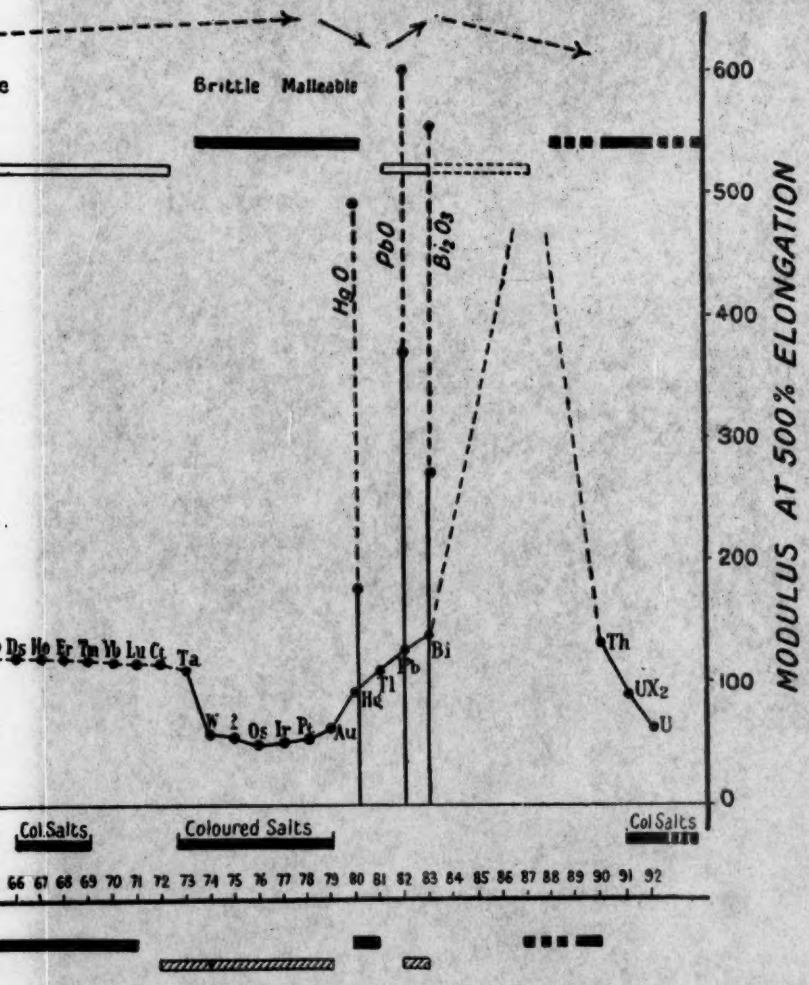


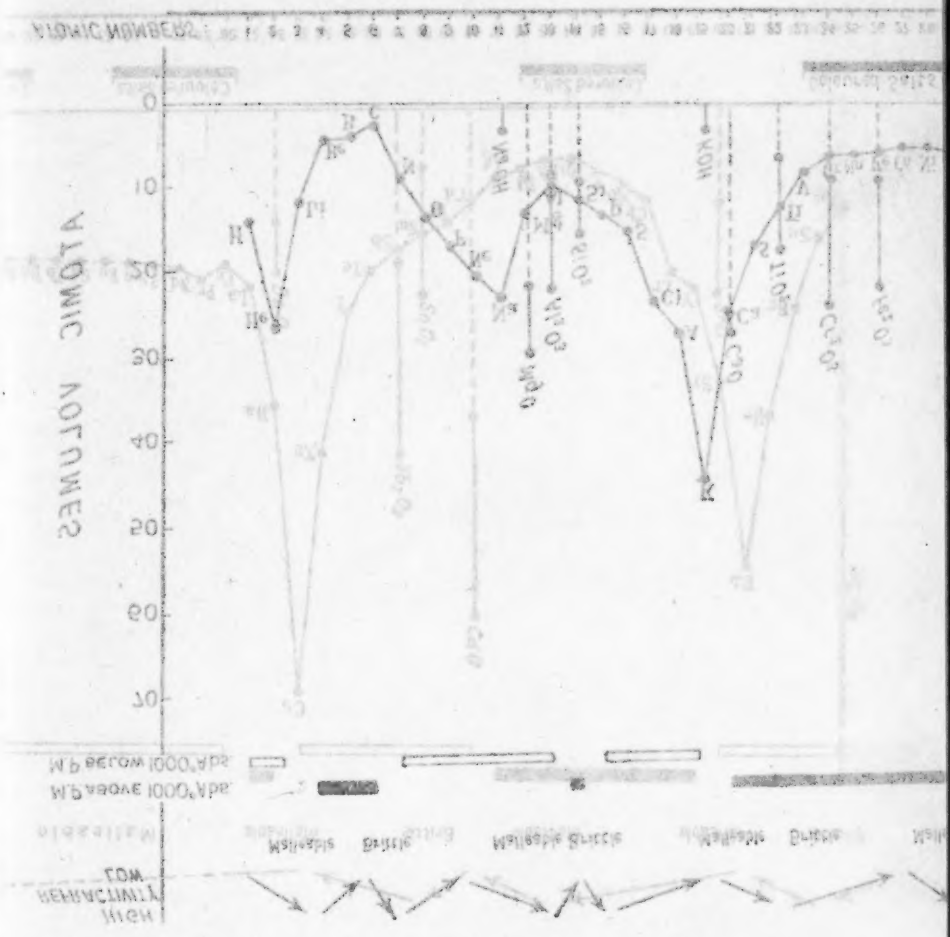
Figure 12—Periodic Recurrence of Activating Properties (Moduli Illustrated Are for Samples Vulcanized 30 Min



c Recurrence of Activating Properties (Moduli Illustrated Are for Samples Vulcanized 30 Min. at 142° C.)


Brittle Malleable
Hg2O
PbO
Bi2O3
MODULUS AT 500% ELONGATION
600
500
400
300
200
100
0
Ta
W
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
UX2
U
Col.Salts
Coloured Salts
Col Salts
66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92

12° C.)



The activity of mercaptobenzothiazole is improved by basic oxides with which it forms salts, and these have been considered the active agents in vulcanization. It has not been found essential for the oxide to be rendered soluble in rubber by means of a fat acid. Although zinc oxide functions best when stearic acid is present, the efficiency of litharge as an activator is independent of the fatty acid.

Metallic soaps are obviously of significance, but their function in vulcanization remains unexplained. It has been suggested that the activity of a metallic soap depends on its solubility in rubber. The following form stearates (*J. Soc. Chem. Ind.* (Japan), **33,** 412B (1930)): aluminum, barium, bismuth, calcium, cadmium, chromium, copper, iron, mercury, magnesium, lead, antimony, tin, strontium, and zinc. This list includes the oxides used in the present work; but, unfortunately, neither the most favorable conditions for the formation of their stearates nor the relative solubility of these salts is known.

Twiss and Thomas (*J. Soc. Chem. Ind.*, **42,** 499T (1923)) found cadmium oxide almost as effective as zinc oxide in promoting the activity of alkyl xanthates, and questioned whether other oxides of the same periodic group would behave similarly.

In studying the results herein presented, it was therefore anticipated that oxides of metals in the same periodic group might show similar activating propensities; but the initial results seemed disappointing in this connection. Although cadmium and zinc oxides had been found to activate dithiocarbamates and xanthates, the oxides of other metals in Group 2 exhibited no activating influence in the presence of these accelerators. When the figures obtained in the systematic work with oxides of metals of Group 2 are illustrated concisely as in Figs. 2 and 3, it is apparent that there is a general tendency for activation with oxides of the Sub-Group B (zinc, cadmium, and mercury), though this is only marked in the case of mercuric oxide with thiurams (with extracted rubber only), basic accelerators, and thiazoles. It was surprising to observe that oxides of magnesium, calcium, and barium exerted little beneficial effect on acclerated vulcanization.

When the mass of data obtained during the second part of the investigation was first considered, there seemed no connection whatever between the position of a metal in the periodic classification and its effect in activating vulcanization in the presence of diphenylguanidine or mercaptobenzothiazole.

It is recognized, however, that the tabular method of showing the recurrence of properties in the elements, first suggested by Mendeléeff, does not satisfactorily expound the periodic principle. A more helpful manner of depicting the scheme is to plot the atomic volumes of the elements against their atomic numbers, as in Fig. 12. Elements in close proximity on the wave-like curve thus produced have properties in common, and there is marked resemblance between elements situated at similar positions on each wave, particularly in the last three periods.

The vertical lines in Fig. 12 represent the magnitude of the load required to give an elongation of 500 per cent to vulcanized rubber samples accelerated with diphenylguanidine (full line) and mercaptobenzothiazole (broken line), respectively, in the presence of the indicated metallic oxides. One cannot fail to notice the poor activating capacity of those oxides whose metallic radicals occur in the descending portions of those waves whose crests are indicated by Na, K, Rb, and Cs; or to overlook the high activating influence of the oxides whose metals appear after passing the troughs of the last three waves. A further observation is that all the early oxides in the graph cause greater activation with a basic accelerator, whereas those in the last period exert their maximum influence in conjunction with mercaptobenzothiazole.

There can be little doubt that there is a close relationship between the atomic structure of a metal and the action of its oxide on vulcanization in the presence of

organic accelerators. The graph illustrated deals only with the mixes containing ordinary raw rubber and two typical accelerators, but critical examination of the data collected indicates a similar trend when employing acetone-extracted rubber or rubber with added stearic acid. Whether similar results would be obtained using accelerators of other classes remains to be investigated. The preliminary work with oxides of Group 2 metals suggests that such is probable.

Summary and Conclusions

1. The activating influence of the oxides of six metals, zinc, cadmium, mercury, magnesium, calcium, and barium in Group 2 of the periodic table, has been investigated with raw and acetone-extracted rubber mixes containing accelerators representative of seven chemical classes.

2. Oxides of barium, calcium, and magnesium exert insignificant activating influence on vulcanization in the presence of all accelerators tested.

3. Cadmium oxide is superior to zinc oxide in activating effect when employed in normal rubber mixes accelerated with zinc isopropylxanthate, tetraethylthiuram disulfide, mercaptobenzothiazole, and ethylideneaniline.

4. Cadmium oxide proved superior to zinc oxide in activating all accelerators tested (other than diphenylguanidine) in a mix made from acetone-extracted rubber.

5. In a mercaptobenzothiazole stock, mercuric oxide gave greater activation than either zinc oxide or cadmium oxide. This superiority was more marked when using acetone-extracted rubber.

6. The activating influence of molar or semimolar proportions of twenty-four metallic oxides on vulcanization in the presence of diphenylguanidine and mercaptobenzothiazole was investigated and reported in the form of graphs showing the rigidity developed after varying times of vulcanization, with mixes containing either raw rubber or acetone-extracted rubber or rubber with additional stearic acid.

7. With mixes containing diphenylguanidine, the activating influence of oxides on vulcanization was more marked the lower the fat acid content. Most oxides gave the highest modulus in a mix containing acetone-extracted rubber and diphenylguanidine.

8. In mixes containing mercaptobenzothiazole, most oxides exhibited an increasing activating influence as the fat acid content of the rubber increased, although in several instances stearic acid in excess of that naturally present in the raw rubber merely acted as a softener.

9. Although development of modulus was retarded by increase in the fat acid content of a diphenylguanidine mix, it was frequently observed that the tensile strength and elongation at break were higher in the presence of stearic acid, suggesting that this improved dispersion of the oxide.

10. Of the twenty-four oxides tested, zinc oxide, cadmium oxide, red lead, and arsenious oxide proved most effective in the presence of diphenylguanidine, arsenious oxide giving greater rigidity than zinc oxide.

11. Bismuth trioxide, cadmium oxide, mercuric oxide, litharge, red lead, and zinc oxide were found satisfactory as activators in mixes incorporating mercaptobenzothiazole; and all the former gave stiffer vulcanizates than obtained with zinc oxide.

12. Cadmium oxide and red lead proved effective with both diphenylguanidine and mercaptobenzothiazole.

13. Cupric oxide showed distinct activating properties, but an equimolecular proportion of cuprous oxide caused such rapid deterioration during and subsequent to vulcanization that it was not practicable to complete physical tests.

14. Experiments directed towards differentiating between activating influence

and inherent accelerating properties of arsenious oxide, red lead, and litharge demonstrated that the exceptionally favorable effects of these oxides on vulcanization may be ascribed mainly to activation of the organic accelerator in a mix.

15. The results are discussed in the light of theories hitherto formulated to explain accelerator action and oxide activation. Evidence is presented that the activating influence of metallic oxides on vulcanization in the presence of organic accelerators is a function of the atomic number of the metallic radical, and may be approximately foretold from a knowledge of its position in the periodic classification of the elements.

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The Influence of the Temperature on the Crystallization of Rubber

H. Dostal

CHEMICAL LABORATORY OF THE UNIVERSITY OF VIENNA, AUSTRIA

It has been found that in the solidification of liquid phases it is frequently necessary to cool or as it is termed, supercool, the system several degrees below the melting point in order to start crystallization. The reason for this is that, because of their relatively great share of the free surface energy (per unit of surface σ), the crystalline nuclei present show a depressed melting point (T_r instead of T), which in the simplest case, *i. e.*, spherical form, can be calculated from the Rayleigh formula:

$$\frac{T - T_r}{T} = \frac{2}{r} \times \frac{\sigma}{s} \qquad (1)$$

where r is the radius of curvature and s is the heat of fusion per unit volume. This same principle applies to the crystallization of rubber,[1] whereby a normal melting point of about 20° to 23° C. is to be contrasted with a melting point of the nuclei of 6° to 8° C. Under pressure and also under tension, both of these melting points, particularly the higher one, are raised.

Since in the case of high molecular rubber crystals the cylindrical form is obviously a better approximation than is the spherical form, the Rayleigh formula assumes a modified form, as follows:

$$\frac{T - T_r}{T} = \frac{1}{r} \times \frac{\sigma}{s} \qquad (2)$$

where r is the radius of a cylinder.

Formula 2 is derived from Formula 1 on the basis that in both cases the relations depend on the differential ratio of the surface of the particles to their volume. A free surface energy of approximately 5 ergs per sq. cm. may be accepted as a correct value (isoprene to air is 22.05 ergs per sq. cm., according to Landolt-Bornsten; the ratio of a crystal to its own fused state is naturally smaller).

Based on an accepted heat of fusion of approximately 6 calories per gram of crystal phase, as obtained in previous experiments, and based on the observed value of T, the depressions of the melting point were found to be those shown in the table below. It will be noticed that the values in the table correspond in an approximate way to the observed range of 14° C. to approximately 30° C. (this latter value is for stretched rubber).

LOWERING OF THE MELTING POINT OF RUBBER

r in Ängstrom Units	$T - T_r$ in Degrees
10	60
40	15
60	10
100	6
400	1.5

It should be remarked at this point that a further means of estimating crystal dimensions is offered by the optical anisotropy effects as measured by Kirsch,[1] in the form of a relation to the wave-length of light. The graphic representation of the anisotropy as given by Kirsch can be interpreted directly on the basis of crystal diameter scattering.

The high state of dispersion of the crystalline phase can be attributed to the fact that in the "fused" state the substance is not actually a liquid. In view of this, and in accord with the data in the foregoing table, no definite melting point of rubber can be assigned.

This is also in accord with the experimentally established fact that there is no one fixed temperature at which crystals and the fused form of the same substance are in equilibrium.[2]

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The Isomerization of Rubber

Cesare Ferri

LABORATORY OF INORGANIC AND ORGANIC CHEMISTRY OF THE UNIVERSITY OF GENEVA, SWITZERLAND, AND THE GIULIANA RONZONI INSTITUTE OF MILAN, ITALY

It is already known that rubber and gutta-percha behave as if they were *cis* and *trans* isomers. Judged by the roentgenographic observations of Meyer and Mark,[1] of Mark and von Susich,[2] and of Lotmar and Meyer,[3] rubber has the *cis* form and gutta-percha, the *trans* form.

Numerous attempts have been made to transform rubber into gutta-percha. As is well known, isomerization from the *cis* to the *trans* form is often induced by light, and for this reason Meyer and Ferri[4] studied the action of ultra-violet radiation on rubber. They were unable to prove that isomerization took place, but rather found a "reticulation" resulting from polymerization. This latter phenomenon was manifest by the irreversible formation of a gel. Sievers[5] obtained the same result by exposing to visible light, with rigorous exclusion of air, a benzene solution of rubber in the presence of a little iodine. Under these conditions likewise, gelatinization took place, without appreciable polymerization.

On the other hand, the technical and patent literature describes a series of reaction products of rubber having physical properties similar to those of gutta-percha; at ordinary temperature they are solids, and at elevated temperatures they become plastic. These substances are formed by treatment of rubber with zinc chloride, toluenesulfonyl chloride, titanium tetrachloride, etc.

We have studied these products by the roentgenographic method. In every case the substance was stretched while hot, and was then fixed in this position by sudden cooling, so that the primary valence chains were oriented parallel to one another, and were immobilized in these positions. That such an orientation was actually attained was indicated by the fact that when the substance so treated was pulverized, cleavage took place in the direction of the fibers.

None of the substances studied gave crystalline interferences, *i. e.*, neither a powder diagram nor a fiber diagram was obtained, but an amorphous ring corresponding to a distance of 5.9 A. U. The regularity of the *cis* chain of rubber thus disappeared, and a chain of molecules of irregular structure was formed, which did not exhibit that characteristic of rubber whereby the latter gives a crystalline lattice when stretched.

It may safely be assumed that, aside from secondary reactions, the reaction is essentially an incomplete isomerization, on some sort of a statistical basis, *i. e.*, within the same chain the *cis* and *trans* bonds alternate in an irregular way. This supposition is confirmed by the fact that, by similar treatment, gutta-percha furnishes products which are scarcely distinguishable from those obtained from rubber. In particular, gutta-percha derivatives give an amorphous ring at the same point as do the corresponding rubber derivatives.

From this it may be concluded that these thermoplastic masses contain a *hydrocarbon intermediate between rubber and gutta-percha.* However, it is not possible at the present time to make any statement as to the respective proportions of *cis* and *trans* bonds.

Besides this transposition, there is also reticulation, *i. e.*, the formation of C—C bonds between two chains, with disappearance of the double bonds. These two

reactions, isomerization and reticulation, result from the activation of double bonds brought about by light or by the catalysts mentioned above.

Titanium tetrachloride has a particularly intense polymerizing influence; by some action similar to that of sulfur chloride, but in a more intense way, a small proportion causes rapid gelation in a very dilute rubber solution. The surface of unvulcanized films of rubber can, in fact, be vulcanized by treatment with a dilute solution of titanium tetrachloride, doubtless by catalytic reticulation.

Preparation of Samples Examined

For the sake of completeness, there are added some descriptive notes on the preparation of the products which were examined roentgenographically; in some cases the methods were obtained from the patent literature.

With Phosphorus Oxychloride.—Crepe rubber was dissolved in phosphorus oxychloride by warming. After 18 hours the product was precipitated by alcohol, was washed successively with alcohol, hot water, dilute ammonium hydroxide, and finally water until neutral. The product was a white powder, containing 1.2 per cent of phosphorus and 7 per cent of chlorine. It swelled in organic solvents. When heated, this powder agglomerated to a thermoplastic mass.

Gutta-percha dissolved partially in phosphorus oxychloride. The product contained 2 per cent of phosphorus and 4 per cent of chlorine. Its properties were identical to those of the product prepared under the same conditions from rubber.

With Chlorostannic Acid.—A 10-per cent benzene solution of milled rubber was refluxed for 3 hours with chlorostannic acid (12 per cent by weight of the rubber). The thermoplastic product obtained after the usual operations had a relatively low viscosity, indicating that considerable degradation had taken place.

Gutta-percha in the form of a 6-per cent solution in chloroform was treated with chlorostannic acid (15 per cent by weight of the gutta-percha). The product resembled the preceding one from rubber.

With Toluenesulfonyl Chloride.—Crepe rubber was mixed with 20 per cent of toluenesulfonyl chloride, and the product was washed.

With Titanium Tetrachloride.—When incorporated without previous dilution, titanium tetrachloride transformed rubber into a friable substance which was not plastic even at elevated temperatures, and which contained a notable percentage of titanium. In solution, titanium tetrachloride coagulated rubber immediately and irreversibly, *i. e.*, reticulation was strongly catalyzed. The product, which was examined roentgenographically, was prepared from a solution of 7 grams of rubber and 0.9 gram of titanium tetrachloride in 100 grams of benzene, which had been allowed to stand for 2 hours. It contained 1.3 per cent of titanium and 2 per cent of chlorine, and swelled in organic solvents.

The corresponding product from gutta-percha was prepared in chloroform solution. It contained 1.4 per cent of titanium. In each case the titanium content was variable, and as shown by specially devised experiments, titanium was not combined chemically with the hydrocarbon. When the products were decomposed by water, the titanium remained in the mass as titanium dioxide.

Acknowledgment

The occasion is taken by the author to show his deep appreciation for the valuable advice offered by Professor Kurt H. Meyer, as well as for the aid given by Mlle. L. Misch, who was kind enough to undertake the roentgenographic experiments.

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An X-ray Study of Stretched Rubber

Henry A. Morss, Jr.

Despite the many attacks which have been made upon it, the phenomenon of the stretching of rubber remains only little understood. Because of the tremendous complications involved, the best approach to the problem seems to lie in finding better quantitative data from which to work. Of especial interest during recent years have been the configuration of the molecule and the changes in its shape during stretching and retraction. This paper aims to report some investigations on this subject.

Experimental

There is some hope of learning in full detail the configuration of the molecule in stretched rubber, because stretched rubber gives an x-ray diffraction pattern which shows the material to be mostly crystalline and there is a possibility of solving the crystal structure. This possibility has been explored.

For the present work a cylindrical camera (diameter 94 mm.) was chosen, with the line of stretch of the rubber lying on the cylindrical axis. In order to get as many high order reflections as possible, the sample was cooled in some exposures to about −120°. All samples were of racked rubber. ("Racking" is stretching to an extensive degree by repeating several times a cyclic process of quick stretching, holding under tension until the sample cools and the stretch "freezes in," and relaxing the stretch in water at about 90°.[1] The x-ray pattern is easily shown to be the same as that of ordinary stretched rubber except that perhaps the "amorphous ring" is reduced in intensity.[2])

The best diffraction pattern of a cooled sample was exposed seven hours (at 15 ma.) to copper radiation filtered by nickel foil. A room-temperature exposure of fifty hours was made in which the radiation was monochromatized by reflection from a rock-salt crystal. This film was made especially in the hope of revealing any weak, low-order reflections which might be masked by the general blackening due to the continuous spectrum present in the nickel-filtered radiation.

Inasmuch as more weak, higher order spots were found when the sample was cooled, all numerical data quoted in this paper refer to the low temperature. Table I gives the positions and estimated intensities of all known spots of the fiber diagram (including two "diatropic" points). Positions are indicated by cylindrical coördinates in the Bernal[3] reciprocal lattice: ζ, the coördinate parallel to the cylindrical axis, which distinguishes the layer lines, and ξ, the radius perpendicular to the cylindrical axis. The values of the radial coördinate are chosen in preference to the more common $\sin \theta/\lambda$, because ξ can be found very easily from the cylindrical films and is most convenient for use in studying the unit cell.

The relative values given in the table should be reliable to within three or four units in the third decimal place for spots on the equator and six or eight units for those on the first and second layer lines. The positions given for spots on the higher layer lines are approximate. The diffuseness and peculiar shape and orientation of the spots make it hard to measure the films very precisely. The absolute values may not be quite so good as the relative ones, because the films were not calibrated carefully enough.

TABLE I

EXPERIMENTAL DATA

Coördinate ξ and intensity are given in body of table
Abbreviations: s, strong; m, medium; w, weak; v, very

Equator (ζ = 0)	First Layer Line (ξ = 0.189)	Second Layer Line (ξ = 0.378)	Third Layer Line (ξ = 0.566)
0.254 s	0.220 vw	0 m	0.254 w
.379 vs	.253 s	0.192 w	.379 m
.508 sm	.378 s	.254 ms	.508 m
.717 sm	.417 w	.377 ms	.717 vvw
1.016 w−	.525 vvw	.419 mw	.758 vw
1.200 w+	.597 mw	.479 w	
1.270 w	.665 vw	.506 vw	Fourth Layer Line (ζ = 0.755)
	.731 w+	.540 mw	0 m
	.766 mw	.595 w	0.379 m
	.912 w−	.657 sm	.508 w
	.968 w−	.726 ms	.717 vw
	1.018 w−	1.10 w	
	1.270 vvw		

Search for Unit Cell

In the search for a unit cell which is consistent with the positions of all the spots observed, the procedure is to calculate the ξ-values of all reciprocal lattice points for a proposed cell and compare them with the observed values. The correct cell will have a ξ-value equal to every one observed.

A natural first try is the generally accepted cell which was proposed in 1928 by Mark and von Susich.[4] It is an orthorhombic cell with axes 12.3, 8.1 (fiber axis), and 8.3 A. U. (The two values 12.3 and 8.3 are twice the plane spacings which give rise to the two very strong equatorial reflections.) For comparison with our table of ξ-values, the values given by Mark and von Susich must be replaced by the corresponding ξ-values, 0.254 and 0.379, from the table. This change makes proper allowance for the fact that the table applies to a cooled sample. With these values assigned, a complete set of ξ-values for the reciprocal lattice of the orthorhombic cell can be computed. It is found that several observed values are not equal, within the experimental error, to any of the computed values. The equatorial reflection at $\xi = 0.717$ is a conspicuous example. Others may be seen in Table II, which includes these data with other possibilities to be described shortly.

A study of all available data shows that two important considerations used in the selection of the orthorhombic cell are correct: the true cell, whatever its form may be, has a fiber axis of length about 8.1 A. U. parallel to the direction of stretch and has its other two axes perpendicular to the fiber axis. The further conclusion that these two axes were mutually perpendicular was drawn by Mark and von Susich from a film made in a Weissenberg camera with a very thin strip of rubber which showed a tendency of alignment of its component crystals parallel to the surface of the strip as well as the familiar "fiber" orientation.

The Weissenberg picture does not require this interpretation. Clearly if the a- and c-axes (let us choose the b-axis as the fiber axis) are nearly but not exactly perpendicular, the picture will not be changed. Actually the angle, which we shall call α, may be considerably different from a right angle. To understand this, consider the arrangement in detail. In the sample which has higher orientation there will be a tendency for the a-axes, say, of all the tiny crystals to align themselves parallel to the surface of the sample. When that occurs, the c-axes will align themselves in two groups, one on each side of the perpendicular to the surface of the sample. The two types are indicated in Fig. 1, in which one set of axes belongs to a crystal having its b-axis along the positive direction of stretch; the other, along

the negative direction. In any sample there will be many of each type. Now if the a-axes of these many tiny crystals are oriented not exactly parallel to the surface of the strip but only roughly so, in order that the c-axes will be distributed throughout the range between the two angular positions shown in the figure, then the beams scattered by the sets of planes which include these axes will spread out continuously over quite a range on the Weissenberg film.

That the Weissenberg film of Mark and von Susich has just such a spread opens the possibility that the angle α may be considerably different from 90°. In a determination of the unit cell, the value of α (and, of course, also the proper indexing of the two independent reflections perpendicular to the fiber axis) remains to be established.

The procedure for an exhaustive study is to assign various sets of indices to these two reflections and in each case calculate the ξ-values of all reciprocal lattice points as a function of the angle α. A range of values from 90° to 115° was considered sufficient to include all reasonable possibilities. Although this calculation was carried through to completion, no thoroughly satisfactory solution for the unit cell was found. Table II gives the dimensions of the two best choices, at room temperature and at the low temperature used. Both have an angle of 109.5° between the sets of planes which reflect the two very strong equatorial spots. The first, which contains sections of eight molecular chains, is just twice as large as the second. While it is consistent with all the diffraction data, it appears too large for the moderate number of spots observed on the film. The second is of the expected size, but does not account for the second layer line spot at $\xi = 0.479$, a spot which is weak but appears to be real. No suitable cell of this size has been found.

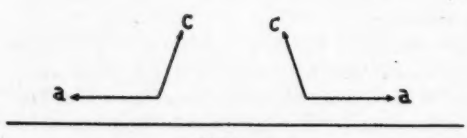

Figure 1

TABLE II

DESCRIPTION OF POSSIBLE CELLS

Cell I (Monoclinic)

	20°	− 120°
a-axis	26.3 ± 0.3 A. U.	25.7 ± 0.3 A. U.
b-axis (fiber)	8.15 ± 0.1 A. U.	8.15 ± .1 A. U.
c-axis	8.9 ± 0.1 A. U.	8.6 ± .1 A. U.
Monoclinic angle β	109.5°	109.5°

Cell II (Orthorhombic)

a-axis	12.4 ± 0.1 A. U.	12.1 ± 0.1 A. U.
b-axis (fiber)	8.15 ± .1 A. U.	8.15 ± .1 A. U.
c-axis	8.9 ± .1 A. U.	8.6 ± .1 A. U.

As far as can be determined from the diffraction data, Cell I may be described equally well as being the same as Cell II with its a-axis doubled. That is, Cell I may be considered to be orthorhombic with axes 24.8, 8.15, and 8.9 A. U. As given, Cell I is monoclinic. Its a-axis has the length 24.8/sin 109.5°. The monoclinic shape given in the table has been preferred because of certain symmetry considerations.

As a result of this relation between the two choices of cell, number I has twice as many ξ-values as number II in the same range of planar spacings. Among these are included all the ξ-values of Cell II.

In Table III are all the measured ξ-values, regardless of the layer line in which they are observed. In the second column are given the nearest calculated values. The value 0.478, which is written in parentheses, belongs only to Cell I. All of the others belong to both cells. The third column gives the best fit with the cell, already described, proposed by Mark and von Susich.

Since this work was completed, a recent paper by Lotmar and Meyer[5] has come to hand. They suggest that the fit is good if the cell of Mark and von Susich is altered by the change of the angle α from 90° to 83.5°. Recalculated for comparison with our data, their best-fitting ξ-values are shown in the last column of Table III. It will be seen that the fit is fairly good except for the two points at 0.540 and 0.729. The discrepancies between these measured values and the nearest calculated ones for the cell of Lotmar and Meyer led us to reject this choice in our study of the possibilities. They are greater than the probable error of measurement of these two spots.

TABLE III

COMPARISON OF CALCULATED AND MEASURED ξ-VALUES

Measd.	Calcd.	Mark, von S.	Lotmar, Meyer
0.192	0.190	0.190	0.190
.220	.219	.228	.215
.254	.254	.254	.254
.379	.379	.379	.379
.418	.421	.426	.414
.479	(.478)	.456	.480
.508	.508	.508	.508
.525	.523	.538	.521
.540	.540	.538	.521
.596	.593	.583	.597
.661	.660	.663	.668
.717	.714	.740	.717
.729	.729	.740	.717
.766	.762	.762	.762
.912	.906	.914	.902
.968	.971	.968	.961
1.016	1.016	1.016	1.016
1.10	1.096	1.083	1.099
1.200	1.199	1.204	1.200
1.270	1.270	1.270	1.270

The indexing of the two strong equatorial spots is shown in Table IV according to the various suggested cells. The column headed "Others" gives the indexing of Mark and von Susich and also of Lotmar and Meyer, except that the notation of the former has been altered by the interchange of their b- and c-axes, to make uniform in the table the assignment of the b-axis as the fiber axis.

TABLE IV

INDEXING OF TWO STRONG EQUATORIAL SPOTS

ξ-Value	Cell I	Cell II	Others
0.254	400	200	200
.379	002	102	002

This discussion of the possible unit cell should not be concluded without mention of an interesting consequence of the choice of angle 109.5° between the two strong equatorial spots. It is that the indexing of all the equatorial reflections suggests,

in so far as they alone are concerned, an effective subdivision of the cell into smaller units each of which contains only a single molecular chain. If this is correct, it probably means that the pattern formed by the projections of the atoms of a molecular chain upon the base plane will be identical for all the chains actually included in the cell and that these patterns will be oriented similarly and will be centered on a regular two-dimensional lattice with axes of 6.6 (=26.3/4) and 4.45 (=8.9/2) A. U. lying at an angle of 109.5°.

The Crystal Density.—A further result from the x-ray analysis deserves attention: the density of crystalline, stretched rubber as calculated from the unit cell. When the angle between the two important sets of planes changes from 90°, the calculated density decreases from the 90° value and comes into better agreement with the best directly measured value. At 109.5° the calculated density is about 1.00. This is much closer to the experimental result of around 0.96 than the calculated value 1.06 for the cell of Mark and von Susich. The cell proposed by Lotmar and Meyer leads to the value 1.05 (calculated from our planar spacing data).[6]

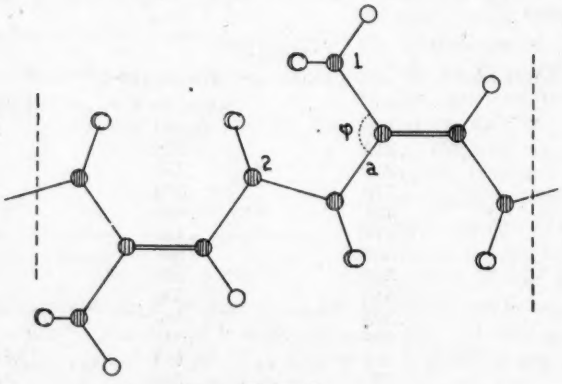

Figure 2

The structural formula of rubber: shaded circles represent carbon atoms; open circles, hydrogen atoms; overlapping open circles represent two hydrogen atoms, one above the other

Thus the cells proposed in this paper appear to resolve satisfactorily a discrepancy which has caused a great deal of discussion.

The Configuration of the Molecule

Disappointed in the hope of solving the crystal structure, we must approach the study of the configuration of the molecule with less complete data than we should have liked. However, the x-ray evidence is clear upon the one point that the carbon atoms of a molecular chain do not all lie in one plane in stretched rubber. This is the only conclusion which can be drawn from a comparison of the measured fiber axis length of 8.15 A. U. and the calculated length of 9.3 A. U. of the two isoprene groups (marked with dotted lines in Fig. 2) which constitute the repeating unit in the molecular chain of rubber. The value 9.3 is based on the structural formula shown in the figure with the single bond length 1.54 A. U.; the double bond, 1.38 A. U.; the single bonds oriented at tetrahedral angles in space; and the double bond along the bisector of the angle between the positions of the two single bonds which it replaces. (That is, the angle φ in Fig. 2 has the value 109.5°, not 120°. This choice is best supported by modern conceptions.[7])

Without violating these restrictions on bond lengths and angles the molecule may have a different configuration if sections of it are moved by rotations about the single bonds joining them to adjacent sections. A careful study of the distances between atoms in the plane configuration hints that there must be such rotations to avoid the very short interatomic distances which that arrangement involves. For if anything like "free" rotation can occur on single bonds, rotation on bond *a* (Fig. 2) should give carbons one and two almost the relative freedom of atoms belonging to different molecules. Consequently, these carbons and their associated hydrogens should not approach markedly closer than similar groups belonging to different molecules in the crystals of other compounds. In the crystals of ethane, hexamethylbenzene, and hexamethylenetetramine the closest approach of carbons belonging to different molecules has been found to be, respectively, 3.64, 3.69, and 3.72 A. U. Further, in such crystals hydrogen has been observed to have a domain radius of 1.29 A. U., or a minimum hydrogen–hydrogen distance of about 2.58 A. U. Actually the separation of the carbons marked 1 and 2 in Fig. 2 based on the plane configuration and the above atomic spacings is only 2.6 A. U., and that of their associated hydrogens, only 1.8 A. U. The comparison shows that such short distances between unbonded atoms are very unlikely to occur. This appears to be sufficient explanation of the non-existence of the plane arrangement.

Thus we conclude that even in stretched rubber the angular positions around the single bonds are not those of the planar arrangement, because of the tremendous repulsions which would be involved. Other authors have pointed out that rotations about the single bonds are almost certainly the changes which take place in the molecule during stretching and retraction. Surely then, as these rotations occur during stretching, they are opposed, at least towards the limit of stretch, by the repulsions which prevent the molecule from assuming the plane form. Probably these repulsions predominate over the whole range of stretch, because the prevailing hydrogen–hydrogen distances in the closest pairs, which will have the most effect, also suggest that the forces are more likely to be repulsive than attractive. Then the end-point of stretch of a molecule is reached when the repulsions just balance the externally applied stress; and the end-point of retraction is the point at which they are balanced by other interatomic forces. This suggestion is at variance with the ideas of Mack,[8] who envisions hydrogen–hydrogen attractions opposing stretch and returning the molecule to its "retracted" shape after the release of stress.

This picture of predominantly repulsive forces increasing as the molecule approaches its configuration in stretched rubber is particularly attractive, because it is consistent with forces of increasing strength near the end-point and is, therefore, a most plausible explanation of the increasing steepness of the outer part of the stress–strain curve.

The kind assistance of Professors J. C. Slater and B. E. Warren is acknowledged with thanks.

Summary

With the more extensive data from new x-ray films of the diffraction pattern of stretched rubber made in a cylindrical camera, an attempt has been made to find the true unit cell. No really satisfactory solution has been reached. The leading possibilities are described. They are characterized by a change of the angle between the two independent sets of planes which reflect the two strong equatorial spots from 90°, the value which first suggests itself, to 109.5°. The new choice is shown to be consistent with all the evidence. It has the great advantage of resolving fairly well the familiar discrepancy between measured and calculated values

of the density of the crystals in stretched rubber. The new value from the unit cell is 1.00.

A necessary consequence of the x-ray data is that the carbon atoms of a molecular chain are not co-planar in stretched rubber. The reason appears to be the large repulsive forces which would have to exist in that configuration. In rotations on the single bonds during stretching and retraction the interatomic forces are probably repulsions in the dominating pairs. Repulsions give a plausible explanation of the form of the outer part of the stress–strain curve.

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Investigation of the Thermal Conductivity of Rubber

L. Frumkin and Yu. Dubinker

PHYSICAL LABORATORY OF THE SCIENTIFIC RESEARCH INSTITUTE OF THE RUBBER INDUSTRY, MOSCOW, U. S. S. R.

The great importance of the thermal conductivity of rubber mixtures in the process of vulcanization, particularly with massive and heavy-walled articles, is generally recognized. Because of the very low thermal conductivity of rubber, the internal and external temperatures of such rubber goods during vulcanization are very different. As a result of this, the outer layers of the article reach the vulcanizing temperature sooner than the inner layers. In the case of massive articles built up entirely of the same rubber mixture, the external layers may be overvulcanized while the internal layers are still undervulcanized. This condition frequently necessitates the use of rubber mixtures having different sulfur and accelerator contents for the innermost and outermost parts of an article. For a rational selection of such mixtures, the distribution of the temperature range within the vulcanized article must be known. The fundamental data for the calculation of this distribution are the thermal conductivities of the mixtures.

The thermal conductivity also is important for the conduction of heat of mechanical goods subjected to frequent succession of deformations (shock absorbers, tires). Furthermore, the thermal conductivity coefficient of rubber mixtures is of considerable theoretical interest, since it is possible to extend our knowledge of the thermal conductivity of disperse systems and its dependence on the magnitude and form of particles and on the physical condition of the rubber.

This communication is confined to a description of the apparatus of the Scientific Research Institute of the Rubber Industry for the exact determination of thermal conductivity coefficients and to a discussion of the results of determinations of these coefficients for a series of rubber compounds.

Most modern methods for the determination of thermal conductivity are based on the determination of the quantity of heat passing by steady flow through a flat, homogeneous slab of the substance under examination. This quantity of heat is determined by the amount of electrical energy required for maintaining the flow.[1,2,3] The determination of thermal conductivity of rubber presents extreme difficulties for two reasons. First, because of its low thermal conductivity, extremely careful measurements are required to prevent the possibility of lateral flow of heat outside the rubber article being tested. Second, the impossibility of raising the temperature above 70–80° C. makes it necessary to work at small temperature intervals, with resulting necessity for greater accuracy of measurement of temperatures and thermal energy transferred.

The number of types of apparatus specially constructed for determining the coefficient of thermal conductivity of rubber mixtures is very small, *e. g.*, the apparatus of Somerville,[4] of Williams,[5] and of Barnett.[3] We consider the first two as insufficiently accurate. The Barnett apparatus, the most recent one described in the literature, is of considerable interest, and was used as a basis for the construction of our installation.

Our apparatus consists of the following two fundamental parts: the heating unit, and the arrangement for measuring the temperature. A general view of the apparatus is shown in Fig. 1.

The heating unit of the installation comprises a welded cylindrical cage (300 mm. in diam. and 50 mm. high), made from sheet iron 3 mm. thick. The cage lid is fastened by 3 bolts passing through the inside of the cage. On the outside of the body of the heater there are welded consoles, by means of which it rests on a wooden support. The flat surfaces of the heater are covered with layers of soft rubber, into which are inserted thermocouples (10 for each surface). The latter are fully exposed on each surface, permitting close contact with the superimposed samples to be introduced later. The large number of thermocouples is required for checking the isothermal conditions of each surface of the rubber sample. In the absence of an isothermal condition, the ensuing lateral flow of heat causes considerable error in the determinations.

Each layer of soft rubber consists of two laminated sheets 2.5 mm. thick. The

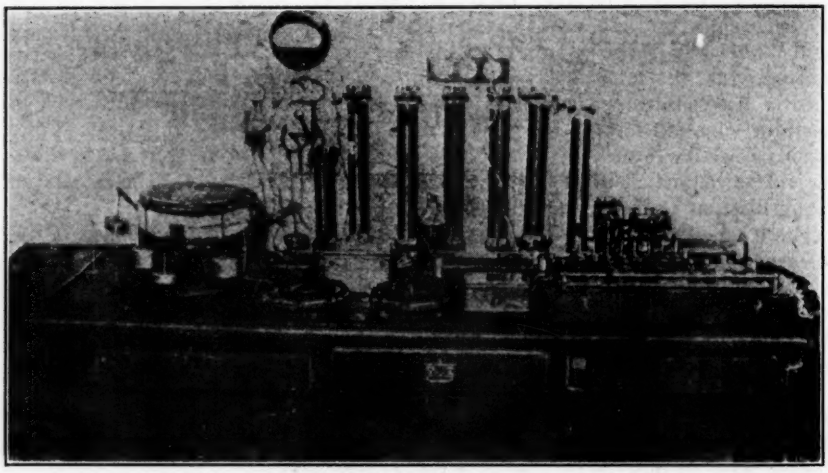

Figure 1

thermocouples are sewed into the inner sheet and the conducting leads are passed between the two sheets. In this way a highly satisfactory insulation of the thermocouple leads is obtained. The same procedure is used for securing the thermocouples to the iron discs laid on the samples. The discs are 300 mm. in diam. and 10 mm. thick. The rubber sheets are cemented to the heater and the discs with Thermoprene. The samples, formed into discs (270 mm. in diam. and 15 mm. thick), are pressed onto the heater surfaces by means of the discs described above. The top disc presses the sample to the heater by its weight and the weight of additional loads suspended from a special iron rim surrounding the disc. The bottom disc presses the sample by the action of loads suspended from the external shoulders of the levers, which have their point of support in the props of the wooden stand.

The interior of the heater cage is fitted with 4 spiral coils fed with city alternating current. Two of these coils, placed above each other close to the cage edges, function as a safety ring, and the other two coils set above each other in the center of

the cage generate the flow of heat, which is accounted for in determining the coefficient of thermal conductivity. The coils are insulated from one another and from the cage walls by asbestos.

In the diametric plane section, shown in the upper part of Fig. 2, the thermocouples are indicated by short arrows. The apparent asymmetry of their arrangement in relation to the axis becomes evident by examining the plan of distribution of the thermocouples, which is given in the lower right corner of the figure. The lateral surface of the heater is covered with asbestos, which facilitates the desired isothermal state of its lower and upper bases.

All the coils are connected in parallel and to the city electric system, and the

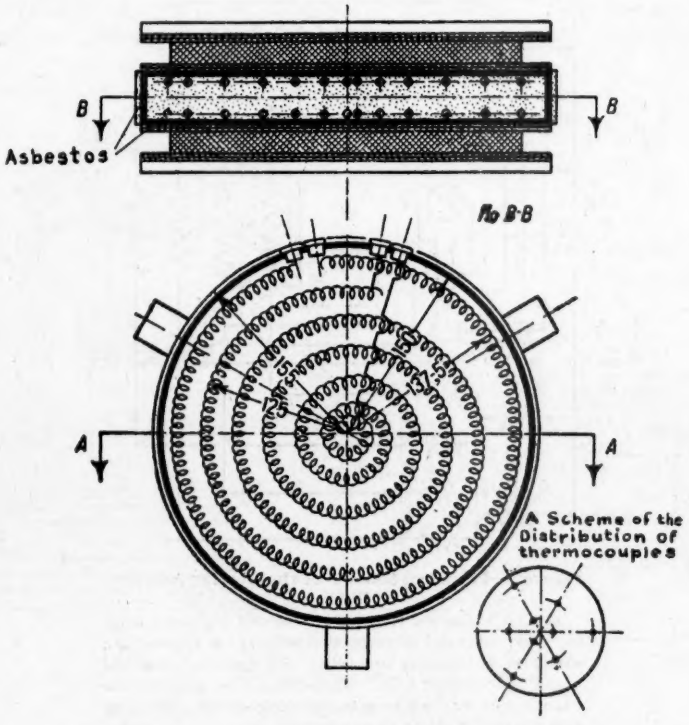

Figure 2—Arrangement of Coils and Thermocouples

heating of each coil is regulated by means of a special rheostat. In addition to the regulating rheostats, the circuit of each pair of heating and safety coils is connected with a rheostat in order to control the current supplied by the city power station and to regulate the temperature. The amount of current consumed by the center coils is measured by the precision laboratory electrodynamic wattmeter calibrated to ± 0.5 watt.

The thermocouple potentials were measured by means of a potential, with a precision to 0.03–0.04 per cent. Calibrated iron-copper thermocouples were used, and the iron leads of the thermocouples were soldered to the heater and discs and connected to the potentiometer clamp by one common lead soldered to the heater. The common cold joint was placed in a thermos bottle. The copper ends of the

thermocouples were connected with another clamp of the potentiometer by means of one of the two mercury commutators, each for 20 thermocouples.

Arrangement of Potentiometer and Thermocouples

Preliminary experiments showed that, because of differences in heat conduction from the top and bottom metal discs the resulting thermal effect in the two rubber samples was somewhat different. This can cause the transmission of heat from one basic heating unit to another, with resultant lowering of the precision of measurements. Therefore subsequent experiments were carried out with only one (top) test-specimen. Under these conditions, the lower heating unit served as a pro-

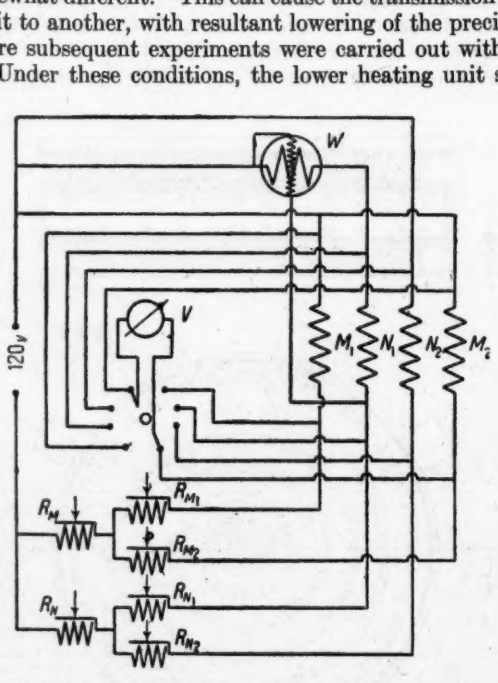

Figure 3—Electrical Scheme of the Heating Arrangement

M_1 and M_2, safety ring coils; N_1 and N_2, basic heating coils; R_M and R_N, special rheostats; R_{M_1} and R_{M_2}, rheostats of the safety ring coils; R_{N_1} and R_{N_2}, rheostats of the basic heating coils. The scheme does not show the commutator for the alternate switching of the wattmeter into the circuit of one or another coil

tecting surface for the top one. By such an arrangement the switching of the wattmeter into the circuit of the bottom heater becomes superfluous, and the entire electric scheme is greatly simplified.

Control of the Installation and Methods of Measurement

The first step in the regulation of the test apparatus was a selection of current strengths for the basic heating coils which, in the presence of samples, would afford an equal degree of heating of the top and bottom surfaces of the heater within 55–75° C. The necessary power was found to be 20–30 watts. For samples of exceptionally poor heat conductivity, the electric energy was reduced by 4–5 watts. From the formula herein given, it follows that for an electric current of given strength the difference in temperature varies in inverse ratio to the coefficient of

thermal conductivity. As could be theoretically expected, the experimental results proved that the difference is increased by lowering the temperature of the hot surface and increasing simultaneously the temperature of the cold surface. During the prolonged time of regulation necessary to obtain a constant flow of heat, the power line potential, of course, varies frequently. These changes are usually equal in each direction, and the resulting difference of temperatures corresponds to a certain mean value of the effective current strength, which is determined by successive readings.

As a next step, a selection was made of the current strengths for the safety ring coils to obtain a constant temperature throughout the entire surface of the heater.

Before proceeding to measure the thermal conductivity of rubber mixtures, the accuracy of determination of the difference of temperatures of the disc and heater was rechecked. To this end the top disc was placed directly on the heater (only

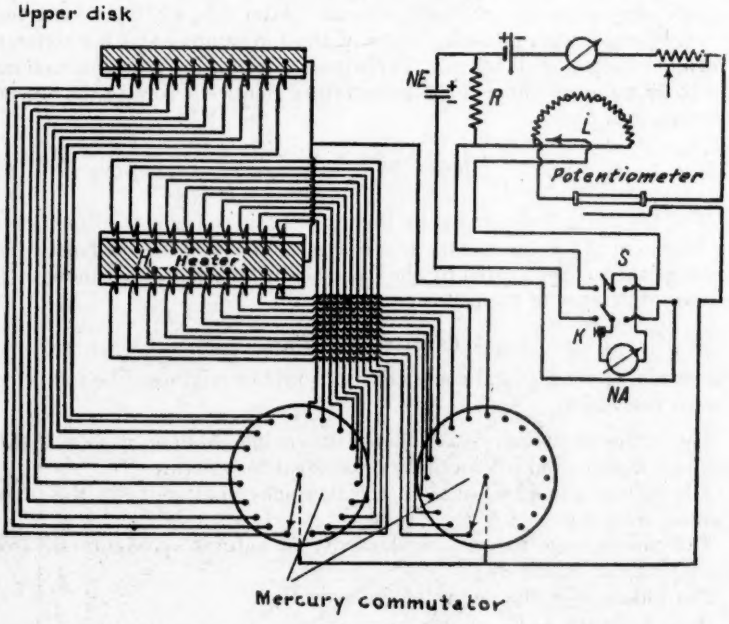

Figure 4

the rubber sheets with sewed-in thermocouples were retained), and the temperature at the point of contact of the disc and heater was measured. The temperatures of the contacting rubber sheets of course are equal; and from the measurements, made by means of the thermocouples sewed into the sheets, it was possible to determine the corrections which must be introduced to account for the action of the disturbing thermoelements formed at the points of soldering of iron conductors to the heater shell and the disc.

Although the determination of the thermal conductivity is made only for the top samples, as shown in the description of the apparatus, another sample of the same composition (equal thermal conductivity) must be fixed to the bottom side of the heater, because only under this condition can the same temperature of both surfaces of the heater be easily attained. In our installation a stationary thermal

effect can be obtained in the presence of rubber samples in approximately 12 hours after heating has begun. In the continuous process of testing, this time can be reduced to 5–6 hours by applying the samples to the heater when it is already hot. Under these conditions it is possible to carry out a determination of the coefficients of thermal conductivity of two different samples in one day, provided that the second sample is charged at the end of the working day.

After preliminary measurements and refining of the methods, the following procedure and method of calculation of results were adopted for the subsequent determinations. After the current has become stationary, the approximate equality of the temperatures of the central and peripheral points of each surface is ascertained. If the difference of these temperatures does not exceed 10 per cent of the temperature difference of the two surfaces, one can proceed with the measurement of the electromotive forces of the separate thermocouples by means of the compensating method, and the results can be computed in temperature on the basis of the preliminary calibration of each thermocouple. After this, a calculation is made of the average temperature of each surface of the top sample, and the difference of these mean temperatures is taken. Three measurements are made on each sample, and the resulting mean value of the temperature is introduced into the formula for the calculation of K:

$$K = \frac{0.2389 \times W \times d}{A(t_2 - t_1)}$$

where W is the wattage dissipated by the upper basic coil; d is the thickness of the sample in sq. cm.; A is the surface area of the sample covering the basic heater, in other words, the surface heated by the basic heater, in square centimeters; $t_2 - t_1$ is the mean difference of temperatures.

Experimental Data

In determining the thermal conductivity of rubber mixtures, the following subjects were considered:

1. The influence of individual fillers (zinc oxide, Maĭkop carbon black, and graphite) on the thermal conductivity of pure rubber mixtures
2. The influence of zinc oxide on the thermal conductivity of the protective and carcass mixtures
3. The comparative thermal conductivity of natural and synthetic (sodium-butadiene) rubber mixtures
4. The influence of the degree of vulcanization.

The influence of individual fillers on thermal conductivity was studied with mixtures of the following compositions:

Smoked sheet	100
Stearic acid	1.5
Diphenylguanidine	1
Sulfur	3
Zinc oxide	5
Filler	5, 10, 20, 30, and 60% by volume, based on the rubber

The fillers were zinc oxide, Maĭkop carbon black, and graphite. As is well known, the first two fillers are active, while graphite is inactive. Therefore it was of great interest to ascertain the effect of the activity of the filler on thermal conductivity. To this end, a comparative investigation of the behavior of zinc oxide and graphite was carried out. In the selection of these fillers, we were guided by the statement

of Barnett that the thermal conductivities of these fillers in a pure state differ but little. According to Barnett, the coefficients of thermal conductivity of zinc oxide, graphite, and carbon black are 0.00167, 0.00217, and 0.00068, respectively.

The results of the determination of the coefficients of the thermal conductivity K of rubber mixtures containing these fillers are given in Table I and Fig. 5.

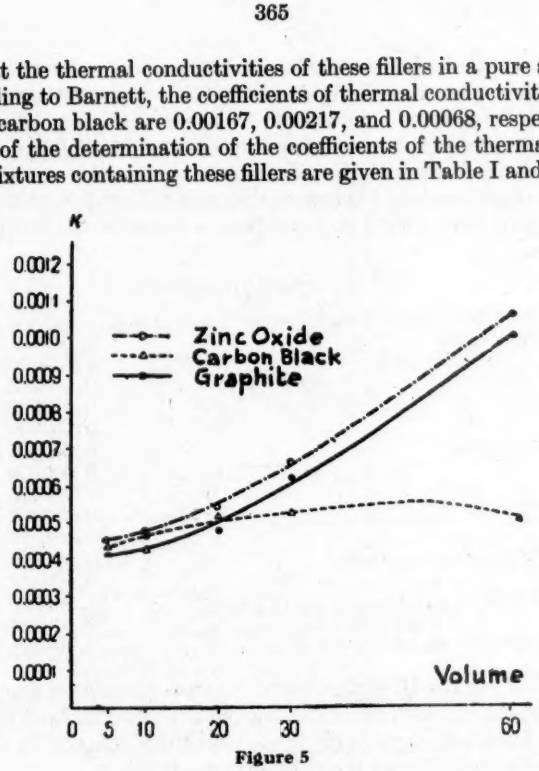

Figure 5

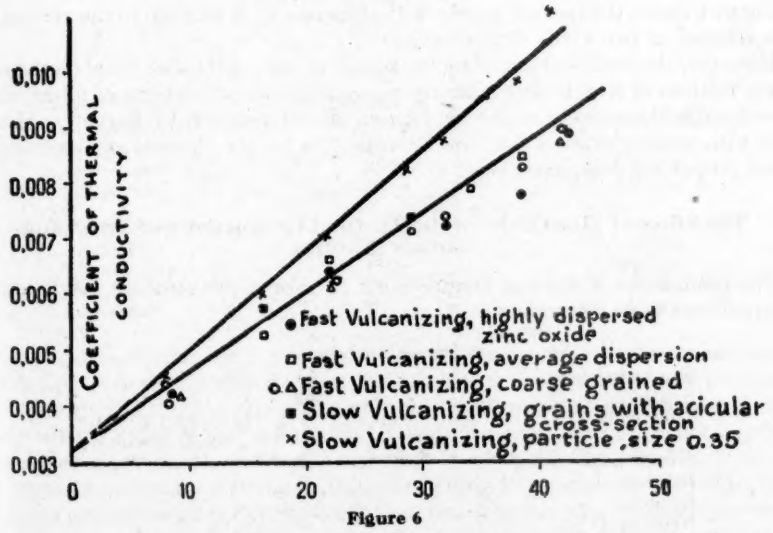

Figure 6

Examination of the results shows clearly that the thermal conductivity of the mixtures containing zinc oxide is somewhat higher than that of the mixtures containing graphite. If the Barnett data on the thermal conductivity of the fillers

themselves are accepted, the results show that the more active zinc oxide imparts to rubber mixtures a greater thermal conductivity than the less active graphite possessing a greater thermal conductivity. Of great interest is the fact that the thermal conductivities of mixtures with graphite and Maĭkop carbon black differ greatly. The thermal conductivity of graphite mixtures is considerably higher. This leads to a consideration of the advisability of a thorough technological investigation of graphite with a view to developing a special treatment for its use as a filler.

TABLE I

Fillers in Percentage by Volume		K
Zinc oxide	5	0.000431
	10	0.000460
	20	0.000522
	30	0.000661
	60	0.001080
Graphite	5	0.000423
	10	0.000469
	20	0.000486
	30	0.000632
	60	0.001020
Maĭkop carbon black	5	0.000428
	10	0.000447
	20	0.000517
	30	0.000536
	60	0.000571

A comparison of our results with those of Barnett discloses a sharp difference in the curves. Barnett obtained a straight-line relation between K and the percentage (by volume) of filler, and accordingly made use of this function in the calculation of the thermal conductivities of fillers by extrapolation.

Figure 6 shows the Barnett graphs of the function K in relation to the percentage (by volume) of two kinds of zinc oxide.

However, the results obtained by us, as well as other published data[6] on the non-linear relation of K of rubber mixtures containing high percentages of fillers, make questionable the validity of the application of extrapolation by Barnett. Hence, it is with utmost caution that the Barnett data on the thermal conductivity of fillers proper are considered here.

The Effect of Zinc Oxide in the Thermal Conductivity of Tread and Carcass Mixtures

The coefficients of thermal conductivity of rubber mixtures of the following compositions were determined:

	Carcass Mixtures
Smoked sheet	60
Synthetic rubber	40
Zinc oxide	7.5, 15, 25, and 40% by wt., based on rubber
Stearic acid	1
Rubrax	2
Rosin	1.5
Neozone D	1
Mercaptobenzothiazole	0.15
K-1	0.6
Sulfur	3.15

Vulcanized at 2 atms. for 45 min.

Tread Mixtures	
Synthetic rubber (plasticity 0.44)	100
Rubrax	8
Stearic acid	4
Zinc oxide	5, 15, 25, and 40% by wt., based on rubber
Maïkop carbon black	55
Neozone D	1
Sulfur	3.5
K-1	0.9

Vulcanized at 3 atms. for 1 hour

The results are given in Table II and Fig. 7.

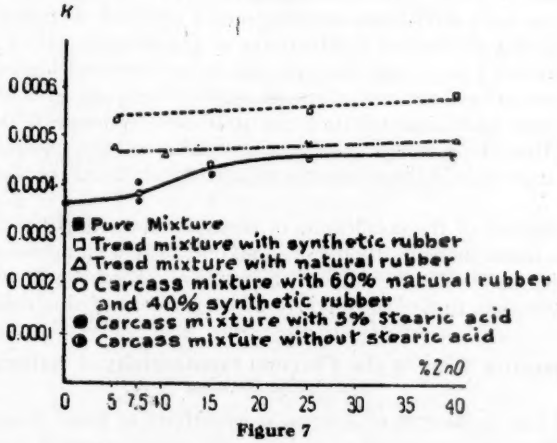

Figure 7

TABLE II

Carcass Mixtures	Percentage	K
Zinc oxide	7.5	0.000375
Zinc oxide	15	0.000445
Zinc oxide	25	0.000451
Zinc oxide	40	0.000469
Tread Mixtures		
Zinc oxide	5	0.000532
Zinc oxide	15	0.000553
Zinc oxide	25	0.000588
Zinc oxide	40	0.000591

The results show that the coefficient of thermal conductivity of the carcass mixtures at first rises slowly with increase of zinc oxide to 7.5 per cent (only by 5 per cent in relation to the K value of the unloaded mixture), then considerably more rapidly with increase of zinc oxide from 7.5 to 15 per cent (by 25 per cent in relation to the pure mixture), and finally more slowly again with increase of zinc oxide from 15 to 40 per cent. For the mixture containing 40 per cent of zinc oxide, the K value is greater by 32 per cent than that of the pure mixture, or only 5 per cent greater than the K value of the mixture containing 15 per cent of zinc oxide. It follows that increase of zinc oxide in a mixture from 15 to 40 per cent (above 3 per cent by volume) has no substantial effect on the coefficient of thermal conductivity.

Such a curve of the dependence of K on the percentage of zinc oxide can be interpreted in the following way. In the vulcanization of a rubber mixture containing zinc oxide in the presence of stearic acid, zinc stearate is formed, the thermal conductivity of which is evidently considerably lower than that of zinc oxide. When the content of zinc oxide is increased, and that of stearic acid remains constant, this effect is less pronounced, because the greater part of the zinc oxide in the mixture is present as such, and therefore the coefficient of thermal conductivity rises uniformly. To examine the validity of this postulated effect of stearic acid on the thermal conductivity of these rubber mixtures, supplementary comparative tests were made with two carcass mixtures containing 7.5 and 15 per cent of zinc oxide, with the addition of stearic acid up to 5 per cent. The coefficients of thermal conductivity of these mixtures proved to be somewhat lower than those of the same mixtures containing only 1 per cent of stearic acid. Moreover, the coefficient of thermal conductivity of the mixture with 7.5 per cent of zinc oxide, containing no stearic acid, proved to be somewhat higher than that of the mixture containing 1 per cent of stearic acid. The coefficients of thermal conductivity of these additional mixtures are indicated by separate dots in Fig. 7. It is believed that these results confirm the validity of the supposition that the proportion of zinc oxide in the mixture is reduced by chemical reaction with stearic acid.

The determination of the coefficients of thermal conductivity of the tread mixtures showed a linear increase, though a small one, in K with increase of zinc oxide from 5 to 40 per cent: The K value of the mixture containing 40 per cent of zinc oxide was greater than that of the mixture with 5 per cent of zinc oxide by only 13 per cent.

Comparative Tests of the Thermal Conductivity of Natural and Synthetic Rubber

To this end the coefficients of thermal conductivity of tread mixtures, differing from the mixtures above described only in the substitution of synthetic rubber for natural rubber, were determined. The results are shown in Table III.

TABLE III

Percentage of Zinc Oxide	K	
	Mixtures Containing Natural Rubber	Mixtures Containing Synthetic Rubber
5	0.000461	0.000532
15	0.000457	0.000553
25	0.000491	0.000558
40	0.000503	0.000591

The tabulated results show that, other conditions being equal, synthetic rubber mixtures are considerably more thermally conductive than natural rubber mixtures, and that the increase in coefficient of thermal conductivity with increase in zinc oxide is approximately equal for the two mixtures. The coefficient of thermal conductivity of synthetic rubber mixtures is higher than that of the natural rubber mixtures by an average of 17 per cent.

The Influence of the Degree of Vulcanization

To ascertain the effect of vulcanization on thermal conductivity, the coefficients of thermal conductivity of unloaded mixtures with various contents of sulfur, carcass mixtures (cured and uncured), and tread mixtures containing natural rubber were determined. The latter were tested before vulcanizing and after vulcanizing with normal and abnormally high percentages of sulfur.

The following formulas were used:

Pure Mixtures

Smoked sheet	100
Sulfur	3, 5, and 10
Mercaptobenzothiazole	1 and 2
Stearic acid	1.5

Vulcanized at 3 atms. for 1 hour

Carcass Mixtures

See the formula on page 366

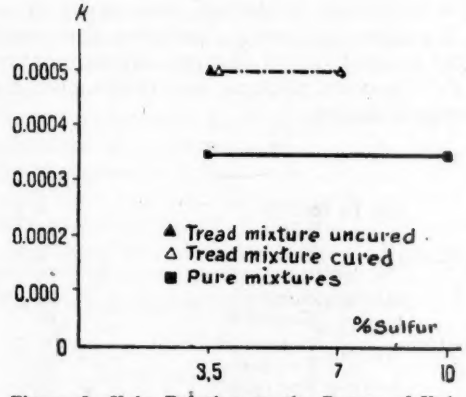

Figure 8—*K* in Relation to the Degree of Vulcanization

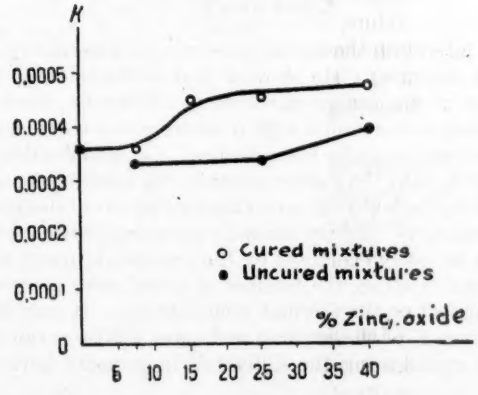

Figure 9—*K* of Uncured and Cured Mixtures

Tread Mixtures

Smoked sheet	100
Sulfur	3, 5, and 7
Rubrax	8
Stearic acid	4
Zinc oxide	40
Maĭkop carbon black	55
Neozone D	1
K-1	0.9

Vulcanized at 3 atms. for 1 hour

The samples of uncured mixtures were prepared by doubling two sheets and covering the surfaces with cigarette paper to prevent adhesion to the surfaces of the heater and discs.

The results are given in Table IV and Figs. 8 and 9.

Figure 8 shows the relation between K and the coefficient of vulcanization for the unloaded and tread mixtures. As can be seen, the thermal conductivity of these mixtures is completely independent of the coefficient of vulcanization and, what is very important, the coefficient of thermal conductivity of uncured tread mixtures is equal to that of the vulcanized mixtures.

Figure 9 shows the coefficients of thermal conductivity of uncured and cured carcass mixtures. For these mixtures the picture is considerably different: The coefficient of thermal conductivity of uncured carcass mixtures is considerably lower than that of the vulcanized mixtures, and, furthermore, the curve points are distributed in a disorderly fashion.

TABLE IV

Mixtures		Per Cent	K
Unloaded Mixtures	Sulfur	3.5	0.000355
	Sulfur	10	0.000355
Vulcanized Carcass Mixtures	Zinc oxide	7.5	0.000375
	Zinc oxide	15	0.000445
	Zinc oxide	25	0.000451
	Zinc oxide	40	0.000469
Uncured Carcass Mixtures	Zinc oxide	7.5	0.000331
	Zinc oxide	25	0.000334
	Zinc oxide	40	0.000392
Tread Mixtures	Uncured with S	3.5	0.000502
	Cured with S	3.5	0.000503
	Cured with S	7	0.000509

It was of great interest to compare these results with the data of Bodger[7] on porosity of rubber mixtures. He showed that unloaded mixtures occlude considerable quantities of air during calendering. However, there is no formation of pores during vulcanization under high pressure and a considerable formation of pores during vulcanization under low pressure. On introduction of certain fillers, such as carbon black, into the rubber mixture, no tendency to form pores can be observed. Therefore, the lower values for the coefficients of thermal conductivity of uncured carcass mixtures (lightly loaded) compared with mixtures vulcanized under pressure can be easily explained by the presence of many minute pores. In the case of the tread mixture, the number of these pores is extremely small and has no perceptible effect on the thermal conductivity. It may be considered that the difference between K of the uncured and cured mixtures can serve to a certain degree as a value representing the difference in porosity between uncured and cured mixtures.

The coefficient of thermal conductivity of one of the experimental samples of ebonite of the "Onazot" type characterized by minute porosity was also determined. The coefficient of this product, d. 0.084, was 0.000187, *i. e.*, about twice as small as that of the unloaded mixture.

Summary

1. The apparatus for the determination of the coefficients of thermal conductivity which is described is satisfactory for the investigation of rubber mixtures.

2. A review of the results of the determinations of K values of various mixtures leads to the following conclusions:

(*a*) The thermal conductivity of rubber mixtures containing synthetic rubber is greater than that of mixtures containing natural rubber.

(*b*) The addition of zinc oxide even in considerable quantities to rubber mixtures containing a large percentage (55 per cent) of carbon black does not substantially increase thermal conductivity.

(*c*) In the case of carcass mixtures a considerable increase in the coefficient of thermal conductivity is observed when the content of zinc oxide is increased from 7.5 to 15 per cent by weight; on further increase in the zinc oxide K increases but little.

(*d*) The K value of carcass mixtures before vulcanization is smaller than that of the same mixtures after vulcanization by an average of 23 per cent.

(*e*) The thermal conductivity of uncured tread mixtures is the same as that of vulcanized mixtures.

(*f*) The coefficient of vulcanization has no effect on the K value of unloaded mixtures and mixtures containing fillers.

(*g*) The K value of rubber mixtures increases sharply with addition up to 60 per cent by volume of fillers with good thermal conductivity (zinc oxide and graphite), but only slowly with the addition of fillers of medium thermal conductivity (carbon black). In other words, the curve of the relation between the coefficient of thermal conductivity and the percentage by volume of graphite and of zinc oxide is convex to the filler axis and is concave in the case of carbon black.

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Comparative Viscometric Studies of Solutions of Crepe Rubber and of Buna

W. Philippoff

KAISER-WILHELM INSTITUT FÜR CHEMIE, BERLIN-DAHLEM

A year or more ago the present author published[1] a review dealing with the viscometric properties of rubber solutions and with methods of measuring these properties. Since that time investigations in this field have been continued at the Kaiser-Wilhelm Institute, and in the present paper an effort is made to show the applicability of these studies to the general problem of rubber. The greater part of the experimentation has been carried out with nitrocellulose solutions as a basis, and it has thus been possible to obtain a fairly definite idea of the nature of these colloidal solutions.

The results of the investigations can be summarized in the following eight points concerning the properties of colloidal solutions.

(1) A method of representing these properties as flow curves, the experimental data and calculations of which are independent of the apparatus and therefore independent of the shearing stress and the mean rate of flow.

(2) The estimation from these curves of the constants, η_0, η_∞, and γ, of a solution.

(3) To be independent of concentration, these material constants can be plotted as functions of the concentration, and from these curves empirical formulas for the material constants can be derived.

(4) These material constants, particularly $[\eta]$, depend on the substance, on the solvent, and on the temperature.

(5) The degree of dispersion has a determinant influence on the course of the flow curve, a relatively flat curve corresponding to a polydispersed substance.

(6) Normally there is no reciprocal effect between individual components in a system, and the viscosity of a mixture can be calculated mathematically from the viscosities of the components.

(7) Different solutions of the same chemical composition and the same viscosity may, nevertheless, give flow curves which differ in direct proportion to the state of dispersion.

(8) On degradation, whether by irradiation, oxidation, or mastication, the state of dispersion remains unaltered, whereas the mean viscosity decreases greatly during such treatment. Consequently, solutions which in their original condition give different flow curves do not after degradation give the same flow curves, *i. e.*, the original differences persist throughout the treatment.

On the basis of these facts, it may be concluded incontrovertibly that the viscosity of a solution depends on the following factors:

(1) The shape of the particles
(2) The state of solvation (combination with liquid)
(3) The degree of polydispersion
(4) The mutual influence of the particles.

The viscometric properties of any substance in a non-aqueous solvent are governed by the magnitude of these individual factors.

With the aid of these experimentally established concepts, a study of the artificial rubber known as Buna was undertaken with a view to analyzing those factors which can be measured in solution by established methods, and which have a determinant influence on the rubbery nature of this product. In principle this can be accomplished by a comparison of the largest practicable number of different substances under various experimental conditions.

In studying this problem, Buna-115 was chosen because, in spite of its being less valuable technically than Buna-N and Buna-S, it has the great advantage of easier solubility. All those who have worked with Buna know well that it is always difficult to make solutions of Buna-N and Buna-S. However, this was of no great concern in the present purely scientific investigation, for it is known, from experiments with nitrocellulose, what properties change in such a series of products, and also in what general manner they change.

With increase in particle size, four properties change:

(1) The viscosity increases
(2) The elasticity in solution undergoes only a slight change
(3) The extensibility diminishes
(4) The film strength increases.

It should be made quite clear at this point what is meant by elasticity. It is the shearing stress or the corresponding modulus of elasticity during tension, *i. e*, the so-called slope. It has no direct relation to the yield point, percentage elongation at rupture, and after-effect (relaxation), just as is the case with steel, the E value of which varies from 1.9×10^{12} to 2.2×10^{12} absolute units, in spite of the fact that its other tensile properties vary within wide limits.

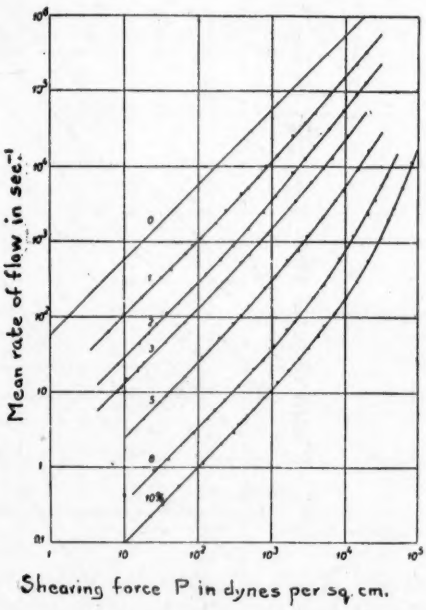

Figure 1
Flow curves of Buna-115 in tetrachloroethane

Experimental Procedure

As already mentioned, Buna-115 in its commercial form was used in the experiments. It was dissolved in a technical grade of tetrachloroethane, which was particularly suitable for the purpose because it is a good solvent of Buna and allows measurements over a wide range of temperatures (its melting point is −40° C., its boiling point, 146° C.). It can also be supercooled very easily, so that measurements of η of the pure solvent can be carried out at −61° C. On the other hand, it has the disadvantage, in common with most chlorinated hydrocarbons, of tending to decompose on storage and on exposure to light, with formation of hydrogen chloride and phosgene. However, as will be shown later, this decomposition has relatively little influence on the experimental results.

A solution of 10-per cent concentration was prepared; this was homogenized for 1 week, was filtered under pressure through a Jena glass frit (G 1), and the solutions to be used in the experiments were prepared by dilution of this 10-per cent solution.

The apparatus employed has already been described. It was a glass viscometer

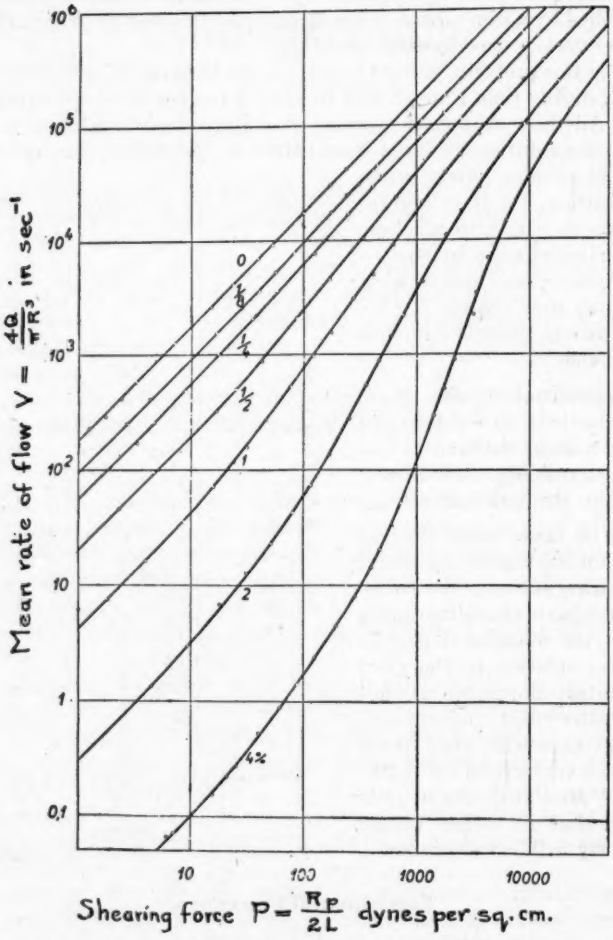

Figure 2
Flow curves of smoked sheet in toluene

with graduated pipette, a pressure bomb, likewise with graduated pipette, and a small overflow viscometer for studying the temperature effects.

Experimental Results

In the initial experiments flow curves were prepared from data on solutions from 1- to 10-per cent concentration (see Fig. 1). Comparative data obtained from similar experiments on smoked sheet are shown in Fig. 2. Qualitatively the groups

of curves in Fig. 1 and Fig. 2 are similar in character, but a more detailed comparison will be made later.

With these flow curves it is possible to derive a relation between η_0 and the concentration, and to complete this relation by measurements at low concentrations down to 0.025 per cent (measured with the overflow viscometer) (see Fig. 3 and Table I). The corresponding curve for smoked sheet is shown in Fig. 4.

The relation between the temperature and the viscosity of 1-per cent solutions of Buna-115 and masticated pale crepe in toluene was also ascertained over a tem-

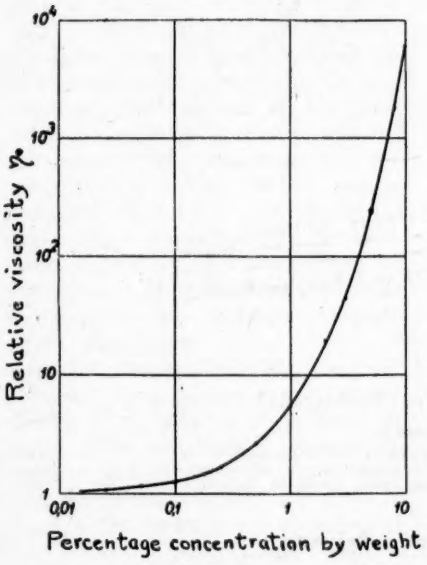

Figure 3
Dependence of the viscosity on the concentration of Buna-115 in tetrachloroethane

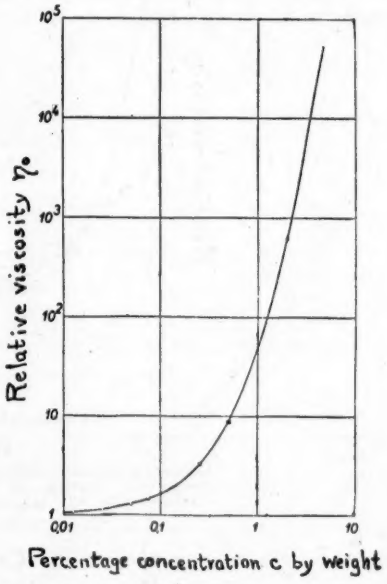

Figure 4
Dependence of the viscosity on the concentration of smoked sheet in toluene

perature range of −80° to 100° C., not studied previously (see Fig. 5). In the measurements from 40° to 100° C., degradation evidently took place, as manifest by an irreversible diminution in viscosity.

To distinguish the reversible temperature coefficient, which in the case of crepe

TABLE I

BUNA-115 IN TETRACHLOROETHANE AT 19.8° C.

C_g	η_{rel}	$[\eta]$
0.025	1.062	2.43
0.050	1.150	2.82
0.10	1.240	2.18
0.25	1.65	2.06
0.5	2.67	2.10
1.0	5.47	1.90
2	19.5	1.80
3	44	1.61
5	245	1.58
8	1800	1.55
10	6000	1.58

and Buna is extremely small, from irreversible degradation, the relative viscosity was measured alternately at 20° C. and at a series of higher temperatures, and the decreases in viscosity were referred to the mean values of the measurements at 20° C. before and after the measurements at the higher temperatures. This is

Figure 5

Dependence of the relative viscosity on the temperature of one-percent solutions of (1) Buna-115 in tetrachloroethane and (2) masticated pale crepe in toluene

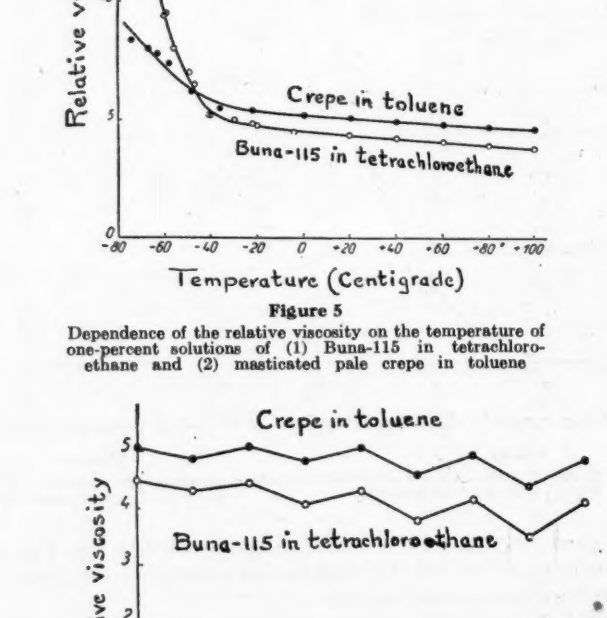
Crepe in toluene
Buna-115 in tetrachloroethane
Relative viscosity
Expt.no. I II III IV V VI VII VIII IX
Temperature 20 40 20 60 20 80 20 100 20

Figure 6

Buna-115 and masticated crepe at elevated temperatures, corresponding to Fig. 5

shown in Fig. 6. The method has already been employed by Busse and Karrer[7] in similar experiments.

The measurements below 20° C. were made with a modified viscometer, which was placed in a Dewar flask with acetone and was brought to the desired tempera-

ture by additions of solid carbon dioxide. The long time required to reach temperature equilibrium had a disturbing effect on the results. Measurements of the solvents were first carried out as nearly as possible within the same temperature range; under these conditions the formula of Andrade[3] relating viscosity with the temperature of pure liquids was found to hold true. The measurements were carried out in such a way that by means of determinations at several shearing stresses it was made certain that in all cases the solutions obeyed the friction law of Newton (evident only within the range of shearing stresses employed).

These measurements show that the small temperature-coefficients of viscosity of Buna solutions and crepe solutions persist down to a temperature of about −40° C. Below this temperature there is a rapid increase in viscosity as the temperature drops, so that the temperature coefficient becomes of the same order of magnitude as that of cellulose derivatives. This temperature of approximately −40° C. in the case of Buna-115, and −50° C. in the case of crepe rubber, corresponds closely to the transformation temperature found by LeBlanc and Kröger[4] and by Kohman and Peek[5] for solid rubber. As qualitative experiments show, Buna-115 actually becomes tough and horny below −40° C. and loses its great extensibility. This proof of a change in the temperature coefficient of solution viscosity might at first thought indicate that the changes which take place at the low temperature are deep-seated, but further experimentation now in progress is necessary to verify this supposition. The curve which is shown indicates complete reversibility.

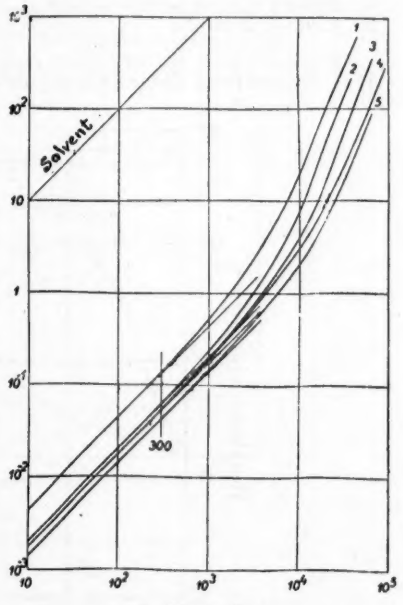

Figure 7

Flow curves of 10-per cent solutions
(1) Masticated pale crepe in toluene
(2) Masticated smoked sheet in toluene
(3) Pyroxylin E-950 in butyl acetate
(4) Buna-115 in tetrachloroethane
(5) Cellit-L in dioxan

Conclusions

First of all from a qualitative point of view, it has been established that the flow curves and the relation between η_0 and concentration of Buna-115 are similar to those of masticated pale crepe. However, a closer comparison shows that the curves of Buna are essentially flatter than those of rubber, although a structure viscosity becomes evident at approximately the same shearing stress. To ascertain whether these similarities between Buna and crepe rubber are accidental or depend on the rubbery properties of each, further experiments were carried out with solutions of the same viscosity, *viz.*, on a 10-per cent (by weight) solution of pyroxylin (E-950 of Wolff & Co., Walsrode) in butyl acetate and on a 10-per cent solution of Cellit-L (I. G. Werk Dormagen) in dioxan. The results of these experiments are shown in the form of flow curves in Fig. 7, while Fig. 8 shows the relative viscosities as a function of the shearing stress. Generally speaking, with all five solutions, the structure viscosity first becomes manifest at approximately the same shearing stress, *viz.*, 300 dynes per cm., beyond which point its character varies

with the particular substance in solution, *e. g.*, the curve of nitrocellulose is the steepest, that of Buna, the least steep. To obtain a more definite measure of the course of these curves, there are shown in Table II the shearing stresses at which the viscosities have diminished to one-half their original values, a relation which has already been identified with the elastic modulus.

TABLE II

Ten-Per Cent Solutions	η_{rel}	Half Value
1. Crepe rubber in toluene	2250	4,000
2. Sheet rubber in toluene	5000	4,600
3. NCE-950 in butyl acetate	5700	7,700
4. Buna-115 in tetrachloroethane	5700	12,800
5. Cellit-L in dioxan	7000	17,000

It is obvious from Table II that rubber is at one extreme and Cellit at the other

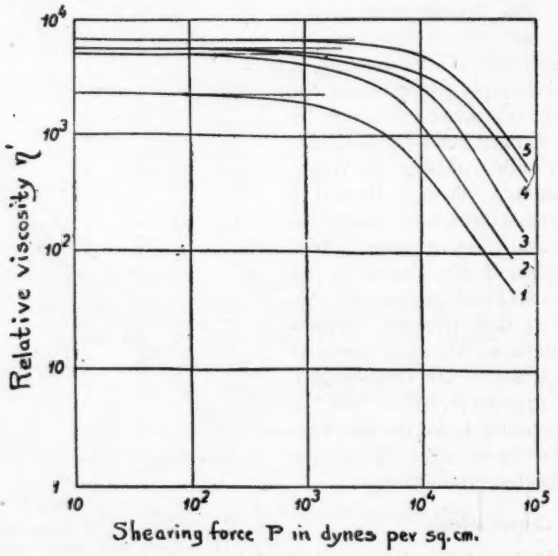

Figure 8

Dependence of the relative viscosity on the shearing force, as derived from Fig. 7. The curves are designated as in Fig. 7

extreme in behavior, with nitrocellulose and Buna intermediate. The moduli of elasticity of these substances do not differ to any great extent, in general 1 to 4 at the most, *i. e.*, much less than in the solid state. This subject will be discussed further at a later time.

Particularly noteworthy is the fact that Buna gives essentially flatter curves than any of the other colloids studied. On the basis of earlier studies of mixtures, the results of which have since been confirmed, this peculiarity of Buna can be ascribed to its state of dispersion. Numerous investigations in America and in Germany have shown that every colloid is composed of particles of various sizes, and judged by its distribution curve contains particles which exceed the normal size of most of the particles. In the limiting case of certain proteins, experiments by Svedberg[6] have shown that the particles are monodispersed; in other words,

the particles are all of the same size. In the case of cellulose,[7] similar investigations with the centrifuge, as well as fractionation experiments, have shown that the majority of the particles are of a definite size but that there is a certain proportion of particles of smaller size, the existence of which may be attributed, at least in part, to degradation. In any case these natural colloids show a rather long "tail" in the curve in the direction of relatively small particles, while the distribution curve falls off rather abruptly in the direction of relatively large particles.

In the case of artificial polymerized substances, including Buna, the end product is formed as a result of chain polymerization, and here numerous investigators, particularly Schultz and Husemann,[8] have shown that the major portion of a polymerizate of this type is composed of particles of rather small particle size, with a "tail" in the curve in the direction of the relatively large particles. This can be demonstrated easily in various ways, *e. g.*, by fractionation experiments.

To this varying character of the distribution curves, which is evident in Fig. 9,

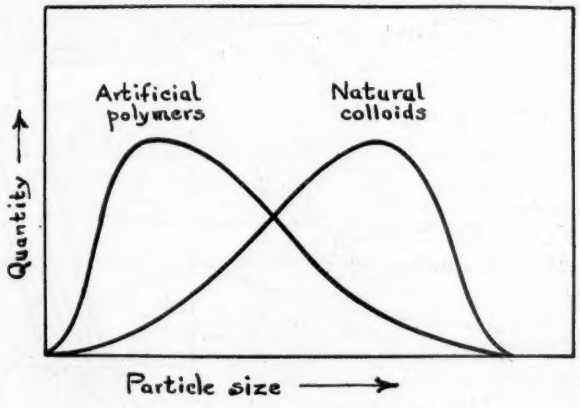

Figure 9
Distribution curves of natural and artificial colloids

can be attributed the varying character of the flow curves; *e. g.*, the small proportion of highly viscous components acquires a structure viscosity sooner than does the main portion.

A comparative examination of the flow curves indicates therefore that differences between different substances in the solid state largely disappear in solution, and that the flow curve of a substance gives a good likeness of the distribution curve, but not of its characteristic rubbery properties.

This noteworthy result will be better understood by considering the relation between modulus of elasticity and concentration, as has been done so thoroughly in the case of gelatin. As is evident from Fig. 10, the S-shaped curve is extraordinarily steep (1:10,000, according to measurement by Poole[9]), particularly in the concentrated region of 30 to 100 per cent, and this is decidedly greater than the difference between solid gelatin and steel, which is about 80, while the difference between lead and gelatin is still smaller, *i. e.*, approximately 1:6.

Since therefore the concentration of a solution plays the predominant role (the curve extends over 11 to 12 powers of 10 in the range studied), the small but technically important changes in the modulus of elasticity in the solid state cannot be determined with any great precision in solution. Curiously enough, in the gel

state, gelatin in water, Cellit in benzyl alcohol, and nitrocellulose in butyl acetate have nearly the same moduli of elasticity. This too lends support to the dominant role played by concentration compared with the relatively small part played by the nature of the dissolved substance.

A consideration of the way in which the viscosity of a Buna solution depends on the concentration will show that the concentration formula which is applicable to rubber solutions is valid only for Buna solutions of concentrations exceeding 3 per cent. At lower concentrations, the viscosity values are disproportionately great, as is also the rule with synthetic polymers such as polystyrene.[10] In Fig. 11, this curve is compared with curves for rubber. Here, too, the considerably flatter trend of the Buna solutions is evident. To what this difference may be

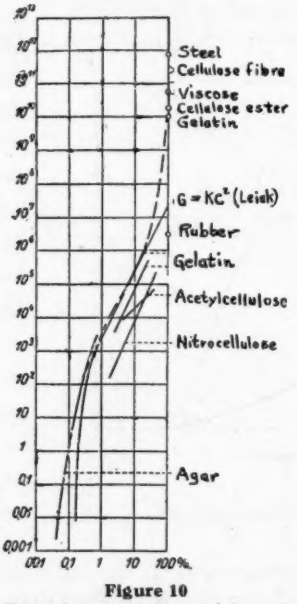

Figure 10
Dependence of the modulus of elasticity of jellies on the concentration, based on data obtained from the literature

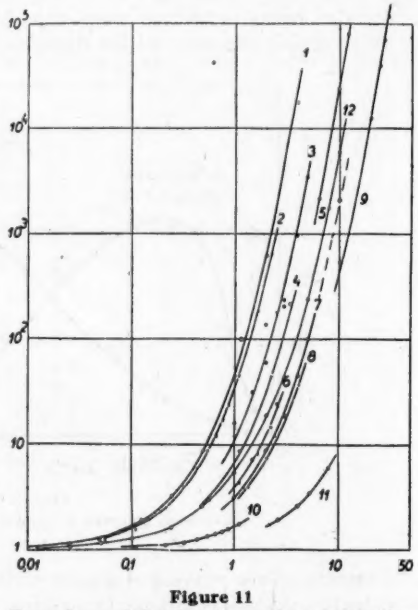

Figure 11
Dependence of the viscosity on the concentration of natural rubber, and Buna-115 (curve 12) for comparison

attributed it is impossible to say at present; perhaps it depends on a state of polydispersion.

The most surprising difference between the viscometric properties of rubber solutions and solutions of cellulose derivatives is the magnitude of the temperature coefficients, as may be seen in Fig. 12.

The curves of nitrocellulose in acetone and of Cellit in dioxan differ to about the same extent as do the curves of Buna-115 and crepe rubber. To decide whether this low temperature coefficient plays a determinant role in the properties of rubber, a curve of polystyrene in benzene, derived from measurements by Danes,[11] is included in Fig. 12. Here again, as with Buna, the temperature coefficient is extremely small, so small in fact that with less careful experiments it could be easily overlooked.

Consequently, the temperature coefficient, at least within the ordinary range of

TABLE III

RELATION BETWEEN CONCENTRATIONS AND η_0 VALUES FOR VARIOUS RUBBERS RECALCULATED ON A BASIS OF $[\eta]$

Curve	Substance	Solvent	$[\eta]$	Experimenter
1	Sheet rubber	Toluene	4.85	Philippoff
2	Crepe rubber	Chlorobenzene	4.20	Fikentscher[a,b]
3	Smoked sheet	Xylene	3.40	Bary and Fleurent[c]
4	Sheet rubber	Pentachloroethane	2.13	Kirchhof[d]
5	Masticated crepe	Toluene	2.00	Philippoff
6	Brominated rubber	Chlorobenzene	1.45	Fikentscher[b]
7	Degraded rubber	Xylene	1.21	Bary and Fleurent[c]
8	Hydrorubber (25,000)	Tetralin	1.11	Mojen[e]
9	Dead-milled rubber	Toluene	0.89	Abernethy[f]
10	Dead-milled rubber	Chlorobenzene	0.53	Fikentscher[a]
11	Hydrorubber (5000)	Tetralin	0.40	Mojen[e]

[a] Fikentscher and Mark, *Kolloid-Z.*, **49**, 135 (1928).
[b] Fikentscher, *Cellulosechemie*, **13**, 58 (1932).
[c] Bary and Fleurent, *Bull. soc. chim.*, [5] **1**, 68 (1934).
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[e] Mojen, *Diss.*, Frieburg, **1935**.
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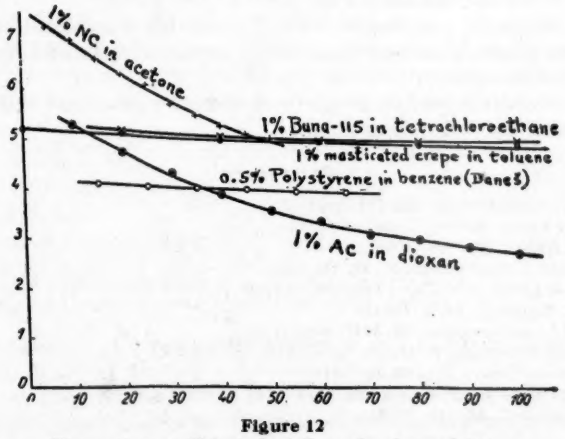

Figure 12
Temperature coefficient of solutions of various substances

temperatures, should not be regarded as a unique property of rubber-like substances. It is probable that at low temperatures polystyrene also shows a similar transformation point. Then again at elevated temperatures polystyrene acquires rubber-like properties. Only by viscosity measurements with other experimental material at low temperatures can a better insight into this problem be obtained.

During the experiments, especially in the measurements above room temperature, deterioration of the solutions had a noticeably disturbing effect on the results. A more thorough study of this has not been yet made because of lack of

TABLE IV

AGING OF A 1-PER CENT BUNA-115 SOLUTION IN TETRACHLOROETHANE AT 20° C.

Days	η_{rel}
0	5.50
3	4.96
19	1.88
29	1.88

time, but preliminary experiments, the results of which are shown in Table IV, indicate that this degradation is accompanied by considerable diminution in viscosity.

This progressive degradation is particularly marked in dilute solutions. Whether it takes place when air and light are rigorously excluded has not been determined, but probably in this respect the behavior of Buna is similar to that of rubber.

It was noticed further that at certain concentrations, *viz.*, from about 0.3 to 1 per cent, the solutions frothed considerably, probably because of a change in surface tension or some similar phenomenon.

Summary

Measurements and their representation as flow curves of solutions of Buna-115 in tetrachloroethane give a means of obtaining an insight into the properties of Buna-115 in solution. By measurements of the viscosity as a function of temperature, it was proved that the temperature coefficient is similar in magnitude to that of natural rubber and that of polystyrene.

A comparison of the flow curves of Buna, masticated rubber, pyroxylin, and Cellit leads to certain conclusions regarding the elasticity of colloids in solution and the role of the distribution curve.

At low temperatures, *i. e.*, below $-40°$ C., both Buna and natural rubber show transformation points, which are manifest by increases in the otherwise very small temperature coefficients.

The measurements reveal no property of natural rubber and of Buna which is peculiar to these two substances alone.

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Water Resistance of Neoprene

Howard W. Starkweather and Herbert W. Walker

E. I. du Pont de Nemours and Company, Inc., Wilmington, Del.

Superior water resistance of well-cured Neoprene, like that of natural rubber, depends upon the absence of water-soluble ingredients and agents that are capable of absorbing water. It has been shown[1,2,3,5] that the water resistance of Neoprene varies greatly with different activating agents. This paper includes a more detailed study of the water absorption of Neoprene–magnesia–zinc oxide compounds and describes certain loaded stocks with improved water resistance. The water absorption was determined by the method already outlined,[5] using slabs 0.20 cm. thick.

Calculation of Water Absorption

The water absorption can be calculated from the increase in weight or from the increase in volume of a stock during immersion in water. A difference between these values is an indication of chemically combined water. This is based upon the assumption that water undergoes no significant change in volume during absorption but that there is a change in volume during a chemical reaction. The two methods of calculating the absorption of water are shown by the equations:

$$\frac{c - a}{a - b} \times 100 = \% \text{ vol. increase by weight method, } W$$

$$\frac{(c - d) - (a - b)}{a - b} \times 100 = \% \text{ vol. increase by vol. method, } V$$

where a = original weight in air, grams
b = original weight in water, grams
c = weight in air after immersion in water, grams
d = weight in water after immersion in water, grams.

If there is no change in volume of the water, $b = d$ and both methods give the same result. If, however, there is a decrease in volume, $d > b$ and the calculated results by the weight method will be greater than those obtained by the volume method. The weight method gives, within the limits of the experimental error, the volume of water absorbed per 100 volumes of sample, and the volume method gives the percentage increase in volume of the sample.

Magnesia Stocks

There is a contraction in total volume during absorption of water by stocks containing magnesia. This contraction varies with the amount of magnesia used but is independent of the zinc oxide content. It is apparently due to hydration of magnesia.

The amount of magnesia hydrated can be calculated from the change in weight in water of a specimen after immersion in water as follows:

	Mol. Wt.	Sp. Gr.	Gram Mol. Vol., Ml.
MgO	40.32	3.20	12.60
H_2O	18.02	1.00	18.02
$MgO + H_2O$	...	..	30.62
$Mg(OH)_2$	58.34	2.36	24.72
		Contraction per gram mole	5.90

$$\text{Wt. MgO hydrated} = (d - b) \times \frac{40.32}{5.90}$$

Parts MgO hydrated per 100 parts Neoprene (M) =

$$(d - b) \times \frac{40.32}{5.90} \times \frac{\text{stock formula wt. with 100 Neoprene}}{a}$$

The results obtained with four different stocks are shown in Table I. Most of the hydration occurs during the first 24 hours; it increases only slightly as the immersion is continued for 420 hours, even though the water absorption continues to increase substantially as shown by the values in the W and V columns of Table I. The average amount of magnesia hydrated is 68 per cent of the total amount which

TABLE I

ABSORPTION OF WATER BY MAGNESIA COMPOUNDS IMMERSED IN WATER AT 100° C.

Formula No.	1					2				
Neoprene Type E, parts	100					100				
MgO, parts	10					20				
ZnO, parts	10					10				
a, grams	5.301					6.103				
b, grams	1.523					1.940				
Hours in Water at 100° C.	c Grams	d Grams	W %	V %	M Grams	c Grams	d Grams	W %	V %	M Grams
24	5.890	1.558	15.59	14.66	5.4	6.925	2.021	19.75	17.80	11.8
48	6.040	1.555	19.56	18.71	5.0	7.089	2.020	23.68	21.76	11.7
72	6.195	1.557	23.66	22.76	5.3	7.220	2.019	26.83	24.93	11.5
120	6.367	1.563	28.21	27.16	6.2	7.372	2.024	30.48	28.47	12.2
330	6.964	1.564	44.01	42.93	6.3	7.774	2.031	40.14	37.95	13.3
420	7.127	1.564	48.33	47.24	6.3	7.884	2.032	42.78	40.57	13.4
Formula No.	3					4				
Neoprene Type E, parts	100					100				
MgO, parts	10					20				
ZnO, parts	20					20				
a, grams	6.011					6.565				
b, grams	1.985					2.327				
Hours in Water at 100° C.	c Grams	d Grams	W %	V %	M Grams	c Grams	d Grams	W %	V %	M Grams
24	6.587	2.027	14.31	13.26	6.2	7.380	2.409	19.23	17.29	12.0
48	6.736	2.027	18.01	16.96	6.2	7.547	2.409	23.17	21.24	12.0
72	6.891	2.025	21.86	20.86	5.9	7.676	2.404	26.21	24.40	11.2
120	7.051	2.030	25.83	24.71	6.7	7.834	2.409	29.94	28.01	12.0
330	7.499	2.037	36.96	35.67	7.7	8.201	2.417	38.60	36.48	13.1
420	7.633	2.037	40.29	39.00	7.7	8.305	2.418	41.06	38.91	13.3

was supposedly added. The magnesia actually used had been on hand for some time. It analyzed as follows:

MgO	61%
$Mg(OH)_2$	35%
$MgCO_3$	4%

Since the determinations of both the degree of hydration and the composition of the magnesia involve indirect calculations, these results are in as good agreement as might be expected. Leaching cannot account for the difference, since water in which samples had been exposed at 100° C. contained only traces of magnesium and zinc.

FIGURE 1

WATER ABSORPTION OF CARBON BLACK STOCKS

15 RUBBER
16 NEOPRENE + PbO
17 NEOPRENE + PbO + MgO + S
18 NEOPRENE + PbO + ZnO + S
19 NEOPRENE + PbO + ZnS
20 NEOPRENE + PbO + CATECHOL

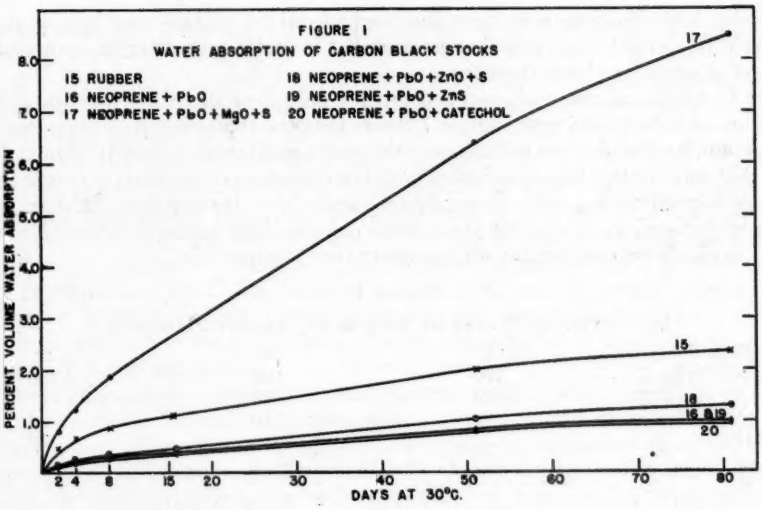
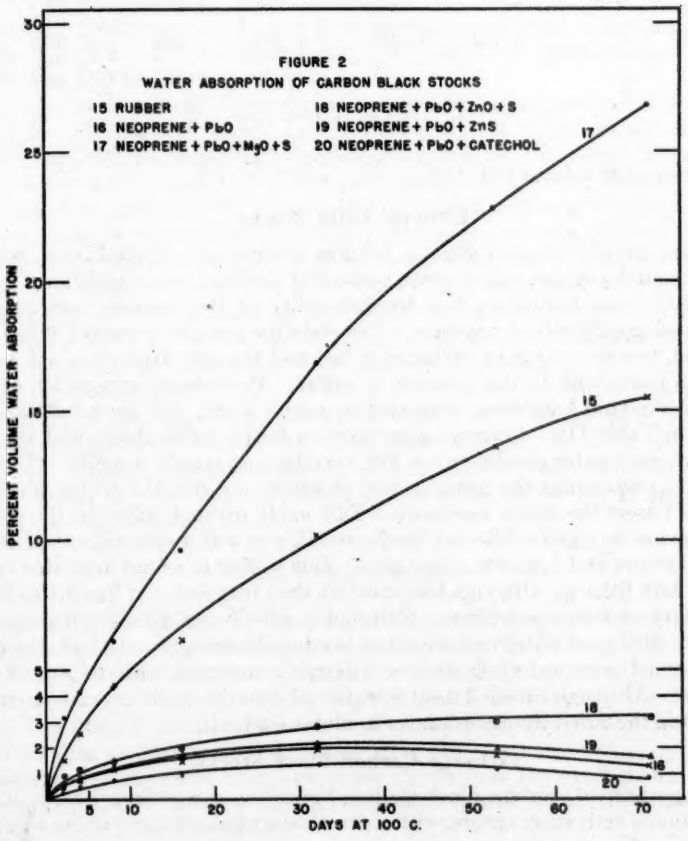


FIGURE 2

WATER ABSORPTION OF CARBON BLACK STOCKS

15 RUBBER
16 NEOPRENE + PbO
17 NEOPRENE + PbO + MgO + S
18 NEOPRENE + PbO + ZnO + S
19 NEOPRENE + PbO + ZnS
20 NEOPRENE + PbO + CATECHOL



Similar determinations with three stocks which did not contain magnesia, as given in Table II, did not show this change in weight in water even after an appreciable amount of water had been absorbed.

The hydration of magnesia can account for only a small part of the water absorption, and the result with sample 7 shows that the replacement of magnesia by magnesium hydroxide does not improve the water resistance. Since it seemed possible that some of this high absorption might be due to small amounts of magnesium chloride formed during cure, silver abietate and silver stearate were included in a series of compounds to convert the soluble chloride into insoluble silver chloride. These stocks failed to show any improvement over the controls.

TABLE II

ABSORPTION OF WATER BY NEOPRENE WITHOUT MAGNESIA

Formula No.	5[a]		6[a]		7[a]	
Neoprene Type E	100		100		100	
PbO	20		20		...	
ZnO	...		10		5	
$Mg(OH)_2$	...		...		10	
Hours in Water at 100° C.	*c*	*d*	*c*	*d*	*c*	*d*
0	4.507	1.427	4.628	1.643	4.842	1.251
24	...	...	...	...	5.372	1.258
48	4.762	1.425	4.866	1.642	5.582	1.255
120	...	...	...	...	5.981	1.255
185	...	...	...	...	6.260	1.258
	Per Cent Volume Absorption					
48	8.2		8.1		20.6	

[a] Press-cured 30 min. at 153° C.

Litharge Gum Stocks

Previous work[3,5] showed that a litharge compound (Eagle-Picher sublimed litharge) containing zinc oxide, rosin, and sulfur had high water resistance. A disadvantage of this combination is the instability of the uncured compound and the processing difficulty it presents. The stability may be improved if the sulfur is omitted, but its activating influence is lost and the zinc oxide does not activate a litharge compound in the absence of sulfur. Possible activators for use in a litharge compound have been evaluated in a gum stock, and the results are summarized in Table III. Litharge alone gives a fairly stable stock, and the cured slabs have good water resistance but low modulus and tensile strength. The addition of magnesia raises the modulus but decreases the stability in the absence of rosin and lowers the water resistance. Zinc oxide without sulfur in the presence of litharge has no significant effect on the stability or water absorption but actually retards the cure and lowers the modulus. Zinc sulfide is a mild activator in combination with litharge, although less effective than magnesia; it has little effect on the stability or water resistance. Catechol is effective in giving a high modulus gum stock with good water resistance but low tensile strength. In fact, the tighter cure obtained with catechol gives a litharge compound with improved water resistance. Although catechol itself is water soluble, the small amounts used probably exist in the cured compound as an insoluble lead salt.

Litharge–Carbon Black Stocks

A comparison of carbon black-loaded Neoprene, compounded with litharge and additional activating agents, with a practical water-resistant rubber compound

showed that the Neoprene compounds, except that containing magnesia, have superior water resistance at 30° and at 100° C. Since two soft carbon blacks (P-33 and Thermax) were used in the rubber stock, both were used in the same proportion in the Neoprene to give the same volume loading. The compounds and test data are included in Table IV.

The water absorption values at room temperature and at 100° C., as calculated from the gain in weight, are plotted against time in Figs. 1 and 2. In each case the water resistance of the loaded Neoprene stock is appreciably better than that of the corresponding gum stock (Table III). The effect is greater than that which can be attributed to the dilution of the Neoprene by carbon black. At both room temperature and 100° C. the water resistance of the stock containing zinc oxide and sulfur is slightly inferior to that containing only litharge as activator. The addition of zinc sulfide has little effect, whereas the addition of catechol actually improves the water resistance.

These conclusions regarding the influence of compounding ingredients on water absorption of the 0.2-cm. slabs were substantiated by measurements made with thinner slabs. The thinner the sample, the greater the apparent water absorption of any given compound, especially during the shorter periods of exposure. For example, the apparent volume per cent absorption of compound 16 during 48-hour immersion in water 100° C. increased from 0.64 to 0.85 to 1.07 as the thickness of the samples varied from 0.21 to 0.14 to 0.08 cm., respectively. The apparent absorption of similar rubber samples (compound 15) under identical conditions increased from 1.92 to 3.02 to 5.65 per cent.

The water resistance of Neoprene compounded with a high amount of soft carbon black, with and without softening agents, was measured to determine the advantage in water resistance to be gained by high loading and the influence of the softening agents on the water absorption. The compounds prepared and the test data obtained are given in Table V. The results show that, although the use of an increased amount of carbon black by itself increases the water resistance, the selection of the softening agent employed to produce a stable and processable stock may decrease the water resistance considerably. This is illustrated by compound 22 in which cottonseed and mineral oils were used. An agent such as Barrett No. 10 oil gives a compound (23) with a plasticity and stability comparable to those of the compound containing cottonseed and mineral oils. During the first 24-hour immersion period at 100° C., Barrett No. 10 oil volatilizes, and the net result is an apparent shrinkage rather than a swelling. After the first 24-hour period compound 23 containing the Barrett No. 10 oil shows a definite swelling, due to water absorption. Upon prolonged exposure, especially at elevated temperatures, the apparent water absorption of all the samples is influenced by loss of material due either to leaching or volatilization.

Effect of Wood Rosin

The effect of the addition of 5 parts of rosin per 100 parts of Neoprene to both magnesia–zinc oxide and litharge stocks is shown by the data plotted in Fig. 3. The addition of rosin makes no difference on the water resistance of Neoprene at room temperature, but it appreciably improves the resistance at elevated temperatures. The litharge stock containing rosin actually appears to be more resistant at 100° C. than at some intermediate temperatures.

Amounts of rosin greater than 5 parts per 100 parts of Neoprene do not improve the water resistance; 10 parts are no more effective than 5 parts, but 20 parts of rosin decrease the water resistance.

TABLE III

LITHARGE GUM STOCKS

Formula No.	8	9	10	11
Neoprene Type E	100	100	100	100
PbO	20	20	20	20
MgO	...	10	...	...
ZnO	...	...	5	...
ZnS	...	...	...	5
Catechol	...	...	...	...
Stability, Plasticity–Recovery Numbers				
Aged at 50° C., Hr.				
0	112–11	153–47	122–14	130–13
24	130–14	168–65	135–13	140–10
48	123–13	179–98	130–16	142–30
96	145–53	190–110	161–48	163–59
Per Cent Volume Water Absorption, 48 Hr. at 100° C., 30-Min. Cure				
	7.6	17.6	7.2	7.3

Stress-Strain Data[a]

Min. of Cure at 153° C.												
10	14(200)	83(1175)	1130	39(550)	121(1725)	1040	11(150)	105(1500)	1200	9(125)	93(1325)	1190
30	25(350)	112(1600)	960	47(675)	155(2200)	1020	19(275)	118(1675)	980	26(375)	134(1900)	1040
60	21(300)	128(1825)	970	58(825)	151(2150)	940	30(425)	128(1825)	970	33(475)	132(1875)	970

Formula No.	12			13			14		
Neoprene Type E	100			100			100		
PbO	20			20			20		
MgO	...			...			...		
ZnO	...			...			...		
ZnS	10			...			...		
Catechol	...			0.1			0.5		
Stability, Plasticity–Recovery Numbers									
Aged at 50° C., Hr.									
0	143–17			111–12			114–12		
24	147–32			133–12			132–16		
48	148–39			139–16			148–50		
96	161–58			155–47			172–64		
Per Cent Volume Water Absorption, 48 Hr. at 100° C., 30-Min. Cure									
	7.6			6.4			5.7		
Stress-Strain Data[a]									
Min. of Cure at 153° C.									
10	21(300)	92(1300)	1100	19(275)	109(1550)	1000	35(500)	97(1375)	890
30	37(525)	135(1925)	1000	42(600)	90(1275)	750	58(825)	111(1575)	730
60	33(475)	142(2025)	1000	54(775)	88(1250)	680	74(1050)	93(1325)	660

[a] The figures for each formula represent stress at 600% elongation in kg. per sq. cm. (lb. per sq. in.), tensile strength in kg. per sq. cm. (lb. per sq. in.), and per cent elongation at break.

TABLE IV

COMPARISON OF CARBON BLACK COMPOUNDS OF NEOPRENE WITH RUBBER

Formula No.	15	16	17
Neoprene Type E	...	100	100
Smoked sheet	100	...	...
FF wood rosin	...	5	5
Litharge	5	20	20
P-33	50	35	35
Thermax	75	52	52
Extra light calcined magnesia	...	...	2
Zinc sulfide (Cryptone)	...	...	...
Catechol	...	...	...
Zinc oxide	...	...	...
Sulfur	1	...	1
"Neozone" A[4]	1.5	...	...
"Antox"[4]	1.5	...	...
"Zenite"[4]	2	...	...
"Retarder" W[4]	0.5	...	...
Stability, Plasticity–Recovery Numbers			
Aged at 50° C., Hr.			
0	140–7	156–13	153–11
24	160–6	188–32	187–36
48	172–11	215–78	212–61
96	191–51	272–128	280–105
Stress-Strain Data[a]			
Cure[b]			
1	69(975) 160(2275) 530	90(1275) 116(1650) 500	92(1300) 107(1525) 520
2	72(1025) 149(2125) 540	104(1475) 118(1675) 420	105(1500) 109(1550) 440
3	74(1050) 149(2125) 520	107(1525) 121(1725) 460	112(1600) 114(1625) 400
4	76(1075) 151(2150) 500	107(1525) 118(1675) 420	118(1675) 118(1675) 400
Stress-Strain Data after Immersion in Water at 100° C.[a]			
Days of Immersion			
2	93(1325) 137(1950) 450	114(1625) 118(1675) 340	116(1650) 116(1650) 300
4	98(1400) 144(2025) 420	121(1725) 121(1725) 300	118(1675) 118(1675) 300
16	100(1425) 141(2000) 430	..... 135(1925) 260	..... 121(1725) 280
32	95(1350) 137(1950) 410	..... 135(1925) 260	..... 116(1650) 280
Per Cent Loss of Material after Immersion in Water at 100° C.			
32	1.88	0.84	1.88

Formula No.	18	19	20
Neoprene Type E	100	100	100

Per Cent Loss of Material after Immersion in Water at 100° C.			
32	1.88	0.84	1.88

Formula No.	18	19	20
Neoprene Type E	100	100	100
Smoked sheet	...	...	...
FF wood rosin	5	5	5
Litharge	20	20	20
P-33	35	35	35
Thermax	52	52	52
Extra light calcined magnesia	...	...	...
Zinc sulfide (Cryptone)	...	10	...
Catechol	...	...	0.25
Zinc oxide	5	...	...
Sulfur	1	...	...
"Neozone" A[4]	...	...	...
"Antox"[4]	...	...	...
"Zenite"[4]	...	...	...
"Retarder" W[4]	...	...	...

Stability, Plasticity–Recovery Numbers

Aged at 50° C., Hr			
0	153–9	155–11	164–14
24	182–39	190–37	241–88
48	213–77	216–79	282–160
96	281–161	274–130	375

Stress-Strain Data[a]

Cure[b]									
1	84(1200)	100(1425)	500	86(1225)	107(1525)	540	102(1450)	111(1575)	410
2	116(1650)	121(1725)	330	97(1375)	118(1675)	460	104(1475)	107(1525)	370
3	104(1475)	109(1550)	400	109(1550)	118(1675)	430	107(1525)	112(1600)	320
4	111(1575)	114(1625)	350	109(1550)	120(1700)	450	116(1650)	123(1750)	330

Stress-Strain Data after Immersion in Water at 100° C.[a]

Days of Immersion									
2	111(1575)	111(1575)	300	111(1575)	114(1625)	400	114(1625)	114(1625)	300
4	111(1575)	111(1575)	300	120(1700)	120(1700)	300	118(1675)	118(1675)	300
16	118(1675)	118(1675)	300	.....	127(1800)	250	.....	127(1800)	250
32	125(1775)	125(1775)	300	.....	135(1925)	280	.....	132(1875)	260

Per Cent Loss of Material after Immersion in Water at 100° C.			
32	1.88	0.89	0.92

[a] The figures for each formula represent stress at 300% elongation in kg. per sq. cm. (lb. per sq. in.), tensile strength in kg. per sq. cm. (lb. per sq. in.), and per cent elongation at break.

[b] Rubber cured 15, 30, 45, and 60 min. at 134° C.; Neoprene cured 10, 20, 40, and 60 min. at 153° C.

Effect of Sulfur

M. A. Youker of the du Pont Company observed that the water absorption of a magnesia–zinc oxide gum stock was increased from 16.1 to 26.7 per cent by increasing the sulfur content from 1 to 3 parts per 100 parts of Neoprene. The influence of sulfur was less marked in the case of carbon black stocks. N. L. Catton of the du Pont Company investigated in more detail the influence of sulfur and observed not only this effect on the water resistance of magnesia–zinc oxide stocks but an even greater effect with litharge–magnesia stocks. In a stock containing 20 parts litharge, 2 magnesia, and 5 rosin, as the sulfur was varied from 0, 1, 3, 5 to 10 per cent the water absorption in 48 hours at 100° C. increased from 7.53 to 11.09, 43.0, 76.2, and 96.5 per cent, respectively. Here again the effect was less marked in a carbon black stock than in a gum stock.

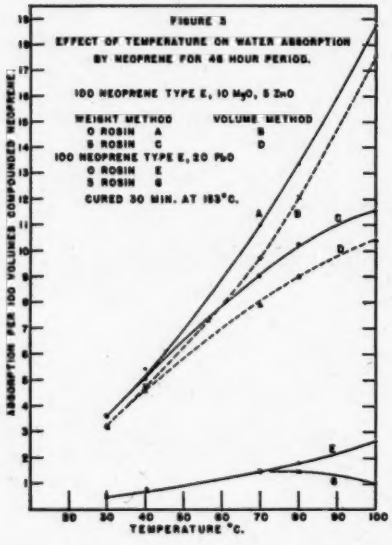


FIGURE 3
EFFECT OF TEMPERATURE ON WATER ABSORPTION BY NEOPRENE FOR 48 HOUR PERIOD.
100 NEOPRENE TYPE E, 10 MgO, 5 ZnO
WEIGHT METHOD
VOLUME METHOD
0 ROSIN A B
5 ROSIN C D
100 NEOPRENE TYPE E, 20 PbO
0 ROSIN E
5 ROSIN G
CURED 30 MIN. AT 153°C.
ABSORPTION PER 100 VOLUMES COMPOUNDED NEOPRENE
TEMPERATURE °C.

This decrease in the water resistance in the presence of sulfur may be attributed to the formation of water-soluble products by reactions of the sulfur with Neoprene. A greater activating influence of litharge as compared with magnesia and zinc oxide on these reactions would account for the greater impairment by sulfur of the water resistance of a litharge compound than of a magnesia–zinc oxide compound.

TABLE V

EFFECT OF SOFTENING AGENTS ON LITHARGE–CARBON BLACK STOCKS

Formula No.	21	22	23
Neoprene Type E	100	100	100
FF wood rosin	5	5	5
Litharge	20	20	20
Carbon black (Thermax)	150	150	150
Cottonseed oil	...	5	...
Mineral oil	...	5	...
Barrett No. 10 oil	...	...	10
Stability, Plasticity–Recovery Numbers			
Aged at 50° C., Hr.			
0	200–14	130–14	130–5
24	250–46	162–7	173–8
48	285–61	189–27	202–30
96	352–116	238–69	270–89

Stress-Strain Data[a]

Cure at 153° C., Min.									
10	56(800)	121(1725)	330	28(400)	97(1375)	260	37(525)	114(1625)	300
20	83(1175)	121(1725)	180	42(600)	121(1725)	290	54(775)	121(1725)	260
40	90(1275)	139(1975)	230	40(575)	121(1725)	290	54(775)	121(1725)	250
60	90(1275)	134(1900)	210	42(600)	125(1775)	250	53(750)	121(1725)	240
Stress-Strain Data after Immersion in Water at 100° C.									
Days of Immersion									
4	102(1450)	144(2050)	190	65(925)	127(1800)	200	86(1225)	132(1875)	200
16	118(1675)	135(1925)	130	93(1325)?	128(1825)	180	104(1425)	127(1800)	160
32	111(1575)	146(2075)	160	67(950)	130(1850)	180	93(1325)	127(1800)	160

	Per Cent Loss of Material after Immersion in Water at 100° C.					
32	0.67		4.84		3.34	
	Apparent Per Cent Volume Water Absorption (Weight Method)					
Days	30° C.	100° C.	30° C.	100° C.	30° C.	100° C.
2	0.14	0.34	0.39	1.87	0.00	−3.76
4	0.23	0.60	0.52	2.47	0.02	−3.40
8	0.29	0.75	0.64	2.77	0.04	−3.25
16	0.33	0.97	0.76	2.75	−0.09	−3.11
32	..	1.17	..	2.00	....	−2.32
51	0.68	0.98	1.26	1.18	−0.35	−2.20
71	..	0.72	..	0.67	....	−2.53
81	0.72	..	1.4	..	−0.72	....

[a] The figures for each formula represent stress at 100% elongation in kg. per sq. cm. (lb. per sq. in.), tensile strength in kg. per sq. cm. (lb. per sq. in.), and per cent elongation at break.

Variations with Temperature

The water absorption for both magnesia–zinc oxide and litharge gum stocks at temperatures from 30° to 100° C. is shown in Fig. 3. These results indicate that the hydration of magnesia occurs at room temperature as well as at elevated temperatures. They show clearly the superiority of the litharge stocks.

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Composition and Structure of Hevea Latex

A. R. Kemp

Bell Telephone Laboratories, New York, N. Y.

MANY properties of rubber are intimately related to the composition and structure of latex from which it is made. Some of these relations, however, remain obscure since our knowledge of latex structure and of the inner properties of rubber is lacking. The purpose of this paper is to help clear up some of the important questions relating to latex and rubber structure and to discuss their possible bearing on rubber properties.

Composition of Ammonia-Preserved Latex

This work and that of F. F. Lucas on ultraviolet microscopy of latex were carried out on commercial ammonia-preserved plantation latex taken from fresh shipments coming from two suppliers. The chemical analyses of these latices are given in Table I and are typical, although the composition of commercial liquid latex may vary somewhat, depending on many causes which will not be dealt with here.

Table I. Analysis of Fresh Ammonia-Preserved Latex

	Naugatuck Latex	Charles T. Wilson Latex
	Per cent based on latex	
Total solids	40.02	40.60
Water and ammonia	59.98	59.40
Acetone extract	2.05	2.04
Water-sol. substances (7)	3.04	2.65
Ash	0.52	0.37
Nitrogen	0.24	0.21
Rubber hydrocarbon (11)[a]	33.98	35.15
Nonrubber hydrocarbon substances	6.04	5.45
Sediment (7)	0.04	0.03

[a] The iodine value was determined by modified Wijs method on acetone-extracted solids after passing several times through tight mill rolls to render it soluble in CS_2.

The composition of commercial bulked latex, however, is fairly uniform from lot to lot since it represents the average product of a large number of trees and tappings. Although it might be said that the study of latex is best conducted on freshly tapped material on the plantation, we must keep in mind that even there the addition of preservatives is necessary to prevent the rapid bacterial changes which freshly tapped latex undergoes after a few hours' exposure to tropical conditions.

These changes are largely prevented by the addition of about one per cent of ammonia. There is no evidence that fundamental changes occur in ammonia-preserved latex under the present methods of shipment and storage in sealed containers for periods up to three months, although some minor chemical changes in serum constituents probably do occur during this period. These changes are more in evidence under improper handling conditions and when the sealed latex container is finally opened.

Composition of Serum

Latex serum contains most of the nonhydrocarbon substances in solution. Analytical data show that the serum of a given lot of 40 per cent latex contains approximately 90 per cent water and 10 per cent of nonhydrocarbon substances in solution. These serum solids appear to be made up mainly of proteins, peptones, amino acids, salts of phosphorus and of the alkaline earth metals, fatty acid complexes, 1-methylinositol, sugars, enzymes, oxidases, peroxidases, etc. Serum substances act as protective colloids in latex, and to the extent that they are retained in crude rubber they influence vulcanization rate, aging, etc. In evaporated latex they remain wholly outside and around the particles as the particles coalesce to form a tough elastic sheet.

Composition of Latex Particles

The latex particles have a strongly adsorbed surface layer of nitrogenous substance, apparently protein, and contain a small amount of acetone-soluble sterol bodies whose location has not been definitely proved. The particles also contain considerable water which fact will be discussed later. The following approximate composition of latex particles has been derived on the basis of information given in the literature and as a result of studies at these laboratories:

Latex Particle Composition	Per Cent by Weight
Rubber hydrocarbon	87.5
Water (Table II)	10.0
Sterol and sterol ester (probably inside particles)	1.2
Protein highly adsorbed on surface	0.3
Fatty acid derivative (transitory layer outside protein layer)	1.0
Calculated particle density, d_4^{20}	0.92

The constancy of the acetone extract upon repeated creaming of latex can be taken as evidence of the presence of an additional layer outside the protein layer on the particles. This layer, however, is removed under extreme centrifuge purification and by treating crepe rubber with concentrated ammonia. It is also removed if the latex is heated with alkali and the rubber coagulated with alcohol (*12*). Under such treatment the acetone extract decreases from about 2.4 to 1.2 per cent with a reduction in its acid number from 109 to

about 11. Under ordinary acid coagulation of latex, free fatty acid is liberated and is found in the acetone extract. This indicates that the fatty acid exists in the latex serum either as a soap or in some form which is easily split upon acidification. The unsaponifiable portion of the acetone extract is found associated with Hevea rubber in fairly constant amount under several conditions of coagulation, centrifuging, or hydrolysis purification studied by the author. This substance, which is apparently made up of a sterol fraction, appears to be present in an amount ranging from 0.8 to 0.9 per cent of the rubber. Sterol esters are also present in small amounts as was shown by Whitby, Dolid, and Yorston (*21*) and confirmed by these laboratories.

The author (*12*) pointed out that a limiting value of nitrogen in Hevea rubber purified by various methods is close to 0.05 per cent, showing the presence of a highly adsorbed film of nitrogenous substance removable only by heating in strong alkali or by other severe hydrolytic treatments. All evidence to date supports the conclusion that this adsorbed layer is a protein although its exact nature is unknown. Certainly its presence on the particle plays an important part in the dispersion of the particle in the serum since its removal with alkali causes flocculation. The author believes it to be different in type from serum protein, since crepe rubber purified by heating at 149° C. under concentrated ammonia still contains 0.05 per cent nitrogen.

The remaining nitrogenous substances in latex are in solution in the serum. About half of this serum nitrogen appears in a heat- and acid-coagulable protein similar in nature to egg albumen which is carried down in the coagulum upon adding acid. The remainder appears in substances which remain in water-soluble form upon acid coagulation and which in part pass out with the serum. Peptones and amino acids have been found in this fraction. If coagulation is brought about under special conditions to avoid precipitation of the serum protein as was done by Belgrave (*2*), the resulting rubber is found to contain only 0.06 per cent nitrogen.

Number of Particles per Gram of 40 Per Cent Latex

Langeland (*13*) recently reported a rubber particle count of 0.64×10^{12} in one gram of latex containing 35 per cent solids, or 0.73×10^{12} for 40 per cent solids. Since he used a magnification of only 400 diameters, it appears from the work of Lucas (page 405) that only the larger sized particles were seen and counted and that this count is far too low.

The number of particles can be fairly accurately calculated if we know their density, shape, and average mass, and the proportion of the total solids they comprise in the latex solids. The serum solids are assumed not to exist as microscopic particles. The work of Kemp (*12*) and Lucas and the data of the present paper lay the foundation for such a calculation:

Shape of particles	Round
Density of particles (d_4^{20}) calculated from composition	0.92
Av. weight of hydrated rubber particles in 1 gram of latex with 40 per cent solids calcd. from hydration and composition data, gram	0.40
Calcd. av. particle mass (from Lucas), gram	0.054×10^{-12}
No. of particles in 1 gram of 40% latex	$\frac{0.40}{0.054 \times 10^{-12}} = 7.4 \times 10^{12}$

As pointed out by Lucas, the average particle diameter of 0.26 micron is probably somewhat too high since particles may exist beyond the resolving power of the microscope used by him. If the weight percentages of these particles were appreciable, their number would be large so that the above calculated count would still be low. However, it is about ten times the direct count recently made by Langeland and more than thirty times the earlier count made by Henri (*10*).

Water in Latex Coagula

Plantation sheets ready for the smokehouse usually contain 20 to 30 per cent water (*15*) whereas crepe ready for drying generally contains 10 to 20 per cent (*16*). Whitby (*20*) gives the moisture content of well-drained crepe as 10 to 15 per cent. De Vries (*19*) recently stated that "the degree of hydration of the particles in the suspended state is not known but probably is not very large, as the particles have distinct contours and are in lively Brownian movement; after discharging and making allowance for serum enclosed in the pores, the amount of moisture in the rubber may be estimated at 10–12 per cent." De Vries, however, gave no supporting data for this estimate.

Recently Piddleston (*17*) showed that the rate of drying of wet sheets became much slower when the water content was reduced to about 10 per cent. These facts lead to the conclusion that water in coagulum in excess of about 10 per cent is held in the coagulum in spaces between latex particles which are not completely pressed together. This water is quickly removed by pressing or by drying, but the remaining water is held more strongly as if it might be water of hydration. The manner in which this residual water is held by the rubber had not been previously investigated.

Residual moisture was determined in various latex coagula after subjecting small samples to repeated high pressures (100 kg. per sq. cm. or higher) or one-minute intervals between sheets of aluminum. The residual moisture exuded after each pressing between foil was removed by lintless absorbent cotton, and the pressing was continued until constant weight was reached. Considerable liquid was exuded in the first pressing; then the weight decreased gradually on additional pressings:

No. of 1-Min. Pressings	Weight of Wet Sample, Grams	No. of 1-Min. Pressings	Weight of Wet Sample, Grams	No. of 1-Min. Pressings	Weight of Wet Sample, Grams
0	1.86	3	0.484	6	0.447
1	0.548	4	0.476	7	0.446
2	0.509	5	0.452	8	0.4455

The moisture in the pressed coagulum was determined by heating it under vacuum at 80° C. to constant weight and the moisture contents given in Table II were calculated on the dry rubber basis. A convenient size sample is obtained by employing 1–2 cc. of normal latex although this can be varied considerably without affecting the results. Pressing is discontinued when the change in weight of the coagulum is not over 0.0005 gram. This point is usually reached after five or six pressings but sometimes requires as many as ten. Larger samples require more pressing than smaller ones to reach constant weight.

The effect of varying the pressure on the coagulum from 100 to 2000 kg. per sq. cm. and of applying the pressure gradually or rapidly upon the residual water content was studied and was found to be without effect on the results. In one case four times the amount of acetic acid needed for coagulation was added without effect on the water content. The use of sulfuric acid in place of acetic tended to give slightly lower values.

TABLE II. RESIDUAL WATER IN PRESSED COAGULA

Latex Employed	Rubber Content	Coagulating Acid Normal Concn.	No. of Tests	Moisture Content Max.	Min.	Av.
				%	%	%
Wilson	40	Acetic	2	11.9	11.0	11.5
Wilson	10	Acetic	2	12.0	11.7	11.9
Wilson	10	Sulfuric	1	....	....	11.2
Naugatuck	10	Acetic	2	11.7	11.1	11.4
Naugatuck	10	Sulfuric	2	11.2	10.5	10.9
Naugatuck[a]	5	Acetic	2	11.0	10.8	10.9
Naugatuck[b]	40	Acetic	4	15.7	14.5	15.3
Naugatuck	10	Acetic	3	15.8	15.3	15.6
Naugatuck[c]	5	Acetic	2	23.3	20.2	21.5
Centrifuged third cream	53	Acetic	1	....	....	17.8
Centrifuged third cream	10	Acetic	2	18.8	17.4	18.1
Deproteinized[d]	5	Acetic	2	23.8	22.7	23.3
Deproteinized	5	Sulfuric	2	20.4	19.8	20.1
Deproteinized[e]	10	Acetic	10	23.8	21.0	22.5

[a] 5% latex heated 2.5 hours at 90° C. before coagulation.
[b] Slightly putrefied latex in bottle 6 weeks before test.
[c] Latex opened and kept for 18 months in can.
[d] 40% latex containing 2% NaOH heated in autoclave 2 hours at 149° C.
[e] 20% latex containing 0.5% NaOH heated in autoclave 2 hours at 149° C., washed in Pfleiderer washer for 10 to 15 minutes, and kneaded from 10 to 15 minutes to remove excess moisture. It was not pressed between foil. This rubber after washing is practically free from proteins and water-soluble matter. When dry it is composed of about 97.5 per cent hydrocarbon; the remainder is acetone extract.

These results show: (*a*) Fresh latex from two sources gives coagula with water of hydration in maximum range of 10.5 to 12.0 per cent. (*b*) After coagulum from one of these latices

stands in a glass bottle for about 6 weeks at room temperature and is occasionally opened, the water of hydration shows an increase. (*c*) Dilution of latex does not result in appreciable variations in results. (*d*) Triple-centrifuged latex cream containing reduced proteins and serum solids yields coagulum with increased water of hydration. A maximum value is obtained from old latex and from latex treated with 2 per cent sodium hydroxide at high temperature to remove proteins and water-soluble substances.

Some residual water may be held by the small amount of residual salts and proteins remaining between the particles, but the data on purified rubber strongly indicate that this must be a small part of the total. How and where, then, can this water be held? The latex particles apparently remain intact on coagulation. They are ash-free and therefore contain no salts to draw water in by osmosis. They are largely composed of pure rubber hydrocarbon whose water absorption is generally considered to be negligible. One hypothesis is that the water is held within the latex particles by sterol bodies which are known to swell strongly in water. Another possibility is that rubber hydrocarbon is actually hydrated.

Further experiments were conducted to determine the effect of several variations in treatment on the water retained by rubber, gutta-percha, and balata. The results of these experiments are given in Table III.

Washed purified rubber is white and opaque after washing, but clear and colorless or pale yellow when dry. Washed Tjipetir white gutta hydrocarbon is high in purity and contains from 9.10 to 9.14 per cent water after washing for various periods from 0.5 to 2 hours. In the wet condition it is white and opaque at 95° C., but when dry it is crystal clear and colorless at this temperature. The results in Table III lead to the conclusion that both rubber and gutta hydrocarbons have the ability to hold water mechanically in some unknown manner within their structure. Rubber can retain a maximum of about 21.5 per cent; the maximum for pure gutta is about 9 per cent. The protein layer on the rubber latex particles seems to have the effect of lowering the water retained in the coagulum. When this layer is broken down by heating the latex alkali or allowing it to stand in contact with air, the retained water increases from an average of about 11.5 per cent to about 21.5, which appears to be the upper limit. It is significant that a substance $C_5H_8 \cdot H_2O$ contains 26.5 per cent water on the dry basis, indicating that such a hydrate is probably not formed. It is more likely that the water is mechanically held in the hydrocarbon colloid structure. The density (d_4^{20}) of both sol and gel rubber hydrocarbons is 0.910; that of gutta is 0.960. This indicates a more closely packed structure for gutta since the hydrocarbons are isomeric. The lower water of retention of gutta is perfectly in line with its closer packing. Although this water appears to be held intermolecularly, further study is needed to decide exactly how it is

held in the hydrocarbon structure. Possibly through studies of light absorption and other properties of these "wet" colloids,

TABLE III. WATER RETAINED BY WASHED RUBBER GUTTA-PERCHA AND BALATA[a]

Material and Treatment	Moisture Content on Dry Basis, %
Crepe rubber heated 3 hr. in concd. NH_4OH at 142° C. and water-washed 5 min.	17.4
Crepe rubber heated 6 hr. in concd. NH_4OH at 142° C. and water-washed 5 min.	18.4
Surinam sheet balata washed 3 hr. in water	11.7
Surinam sheet balata deresinated and water-washed 3 hr.	7.4
Tjipetir white leaf gutta-percha water-washed 1 hr. (not pressed)	11.7
Tjipetir white leaf gutta-percha water-washed 2 hr. (not pressed)	11.7
Tjipetir white leaf gutta-percha water-washed 2 hr. (pressed)	9.1

[a] All samples were machine-washed. A laboratory corrugated roll washer was used for the rubber, and a laboratory gutta-percha roll washer was used for the gutta-percha and balata. Gutta-percha and balata samples were pressed only once to a very thin sheet before moisture was determined.

it will be possible to obtain added information regarding their structure and the manner in which they hold water. The data on balata in Table III indicate that the resins which are largely sterol bodies are capable of retaining considerably more water than the hydrocarbon.

In the treatment of crepe with concentrated ammonium hydroxide, it appears that the water content rises to about the same value as is obtained in the case of triple-centrifuged latex. These data and those in Table II indicate the possibility that both the serum and the adsorbed protein play a part in controlling the water content of the latex particle. The author can only speculate at this time on the underlying causes for the variations found.

The semifluid nature of the inner contents of the latex particle as noted by Freundlich and Hauser (*8*) may indicate that there is an emulsion of hydrocarbon within the particle. On the other hand, this fluidity may possibly be explained on the basis that the particles contain hydrocarbon in a low state of polymerization which increases upon removal of moisture. Further study of latex particles is needed to answer this question.

Structure of Latex Particles in Hydrocarbon Phases

Hauser (*9*), by microscopic studies involving micromanipulation, came to the conclusion that the particles are predominately nonspherical and consist of a hard elastic shell containing a viscous nucleus. Observation of these particles by Lucas under a high-powered microscope using ultraviolet light shows them to be round, except where flocculation or distortion effects are involved. Freundlich and Hauser's concept (*8*) that there is a tough elastic gel hydrocarbon shell on the particles with a softer and more easily distensible sol hydrocarbon center appears reasonable on the basis of present experimental evidence.

Since there is not enough protein to form a tough shell on the particle and since the skin appears to be highly elastic, the only conclusion is that it must be composed of rubber hydrocarbon. Ultraviolet photomicrographs (λ 2573) show that the particle is nearly transparent.

It is well established by the work of Caspari (*4*), Feuchter (*6*), and others that the rubber hydrocarbon in unmilled plantation sheet or crepe rubber is only partly soluble in petroleum ether and that this soluble fraction called "sol" rubber is softer and more elastic than the less soluble portion called "gel" rubber. The author has on many occasions confirmed the existence of these two forms of rubber in laboratory investigations extending over several years.

The diffusion process with petroleum ether has been frequently used to prepare pure sol rubber. After studying all other methods, the author has reached the conclusion that the diffusion procedure conducted at room temperature offers the best available method to prepare pure sol rubber hydrocarbon. Crepe rubber is generally used, and the resin is completely removed by repeated extraction at room temperature with a mixture of 2 parts of acetone and 1 part of petroleum ether boiling at 35° to 60° C. This solvent is then replaced by the pure petroleum ether to dissolve the soluble hydrocarbon. One hundred cubic centimeters of solvent are used for each gram of rubber. Crepe rubber swells to a maximum degree after standing for several hours, during which time the more soluble hydrocarbon portion diffuses out. This portion is removed by careful decantation of the solution from the swollen gel and replaced by fresh solvent. As this procedure is repeated, it is found that less and less rubber is found in solution. Over extremely long periods it was found in a particular case that all but 17.4 per cent of crepe rubber dissolved. The nitrogen content of the original crepe rubber was 0.42 per cent and that of the gel residue was 2.49 per cent, showing that practically all the nitrogenous matter is left in the gel residue. If the solvent is carefully removed by a stream of carbon dioxide at room temperature to avoid oxidation, each hydrocarbon fraction is colorless and crystal clear, is ash- and nitrogen-free,

and analyzes exactly C_5H_8. Each succeeding soluble fraction becomes gradually tougher and less elastic, showing definitely that the rubber hydrocarbon in Hevea is not composed of two distinct hydrocarbons—namely, sol and gel—but of a series of hydrocarbons of increasing toughness and decreasing solubility in petroleum ether. Density and refractive indices were determined on various sol fractions, and they were all found to be the same within experimental error. Density values ($d_4^{25°}$) varied from 0.905 to 0.910. The highest is believed to be the most reliable. Refractive indices ($n_D^{25°}$) varied from 1.5214 to 1.5217. These values compare closely with those for whole rubber hydrocarbon found in the literature, showing that sol and gel rubber have the same density and refractive index.

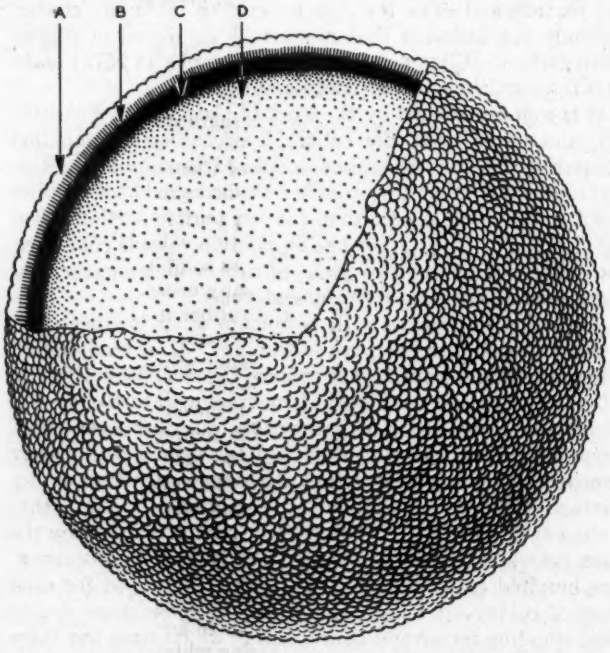

FIGURE 1. STRUCTURE OF RUBBER LATEX GLOBULE

A. Transitory layer of soap or lipide
B. Adsorbed protein layer
C. Gel rubber hydrocarbon layer
D. Sol rubber hydrocarbon emulsion containing sterol bodies

Rubber can be radically altered in physical properties without change in density or refractive index. For example, 10 grams of crepe rubber were refluxed for 5 hours in 200 cc. of tetrachloroethane, the solvent was distilled off with a stream of carbon dioxide, and the last traces were removed under high vacuum. The residue was liquid rubber similar to a heavy oil and completely soluble in petroleum ether (boiling point 35°

to 65° C.). Its iodine value showed a 92.5 per cent unsaturation, its $d_4^{25°}$ value was 0.9224 and $n_D^{25°}$ 1.5210. Macallum and Whitby (*14*) found the density and refractive index of smoked sheet at 20° C. to be 0.9217 and 1.5208, respectively. Oxidation undoubtedly accounts for the physical breakdown of this rubber which, however, has practically no effect on its density or refractive index.

The difference in physical properties of sol and gel rubber hydrocarbons has been explained on the basis that the gel is a higher polymer as determined by molecular weight methods, such as the Staudinger viscosity procedure. This difference in molecular weight as determined by viscosity may be questioned since it is difficult to disperse the gel hydrocarbon in solvents completely. The difference may be ascribed to one of colloidal state. If 25 cc. of pure propionic acid are added to 0.2 gram of the "insoluble" gel which is swollen in 75 cc. of carbon disulfide, the gel rubber disperses completely on standing for 1 or 2 hours. It is possible, however, that this gel-sol transformation is the result of oxidation.

Figure 1 is the author's conception of the structure of the latex globule on the basis of existing information and is offered only for its suggestive value.

Effect of Milling on Particle Structure in Sheet Rubber

That in evaporated latex or plantation sheet rubber we are dealing with a particle structure seems undisputable from the accumulated evidence of many investigations. As latex dries under the microscope, we can see the various sized particles flocculate and strongly cohere without losing their particle outline. No evidence of porosity of sheet rubber exists, indicating that the particles in this material must fit together perfectly. The particles apparently do not burst on coagulation, with the inner content flowing out to form a continuous hydrocarbon phase. On the contrary, dielectric measurements and water absorption studies show the presence of a continuous serum solid phase between the particles (*12*).

Van Rossem (*18*) viewed the plasticizing effect as the bursting of the particles, with the result that their soft plastic contents become the continuous phase. This might appear to be a reasonable explanation, were it not for the fact that rubber breaks down only slowly, if at all, when worked out of the oxygen contact. Busse (*3*) showed that plasticization requires oxygen and that mastication in air and ozone is an oxidation process. After milling, rubber disperses freely and completely in light petroleum solvents. This leads to the view that the tough gel skin on the particle is changed to a plastic form under the oxidizing and heating influences of milling. This change would take place most rapidly on the particle surfaces which are freely exposed to air and ozone during milling. The total amount of oxygen taken up during a half-hour breakdown on a cool laboratory mill is so small as to

be undetectable by ordinary analysis. However, in certain hydrocarbon polymerization reactions oxygen can function either as a polymerization or depolymerization catalyst. Busse (*3*) showed that peroxides are formed in rubber during milling. Whether this peroxide formation in the hydrocarbon plays a primary or secondary role in the softening and plasticization effect on milling has not been proved. It is possible that hydroxyl groups are first formed, as is the case in most hydrocarbon oxidations.

Hopkinson sprayed latex rubber breaks down more slowly than plantation sheet; this is explained by the fact that sprayed rubber contains a larger amount of antioxidant which protects the particles. In this same connection it is known that rubber, freed from serum solids and antioxidant by coagulating it from highly diluted latex, breaks down quickly on the mill because of its more rapid oxidation.

In presenting these views which are in some ways similar to those of Bary and Hauser (*1*), possibility of the bursting particle mechanism of plasticization is not forgotten. However, on account of the extremely small size of these particles their bursting under milling does not seem likely (*5*). The fact that oxygen is essential to the plasticizing process makes the gel-to-sol conversion mechanism through oxidation and heat seem best to fit the facts.

Acknowledgment

Much of the experimental work given in this paper was carried out by H. J. Peters.

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Ultraviolet Microscopy of Hevea Rubber Latex

Francis F. Lucas

BELL TELEPHONE LABORATORIES, NEW YORK, N. Y.

THIS paper is a report of studies made on two bulk samples of commercial rubber latex by means of the ultraviolet microscope. This apparatus does not appear to have been used to an appreciable extent for the study of the rubber latex particle. Green (*1*) applied it to vulcanized rubber latex and apparently made some observations on unvulcanized latex.

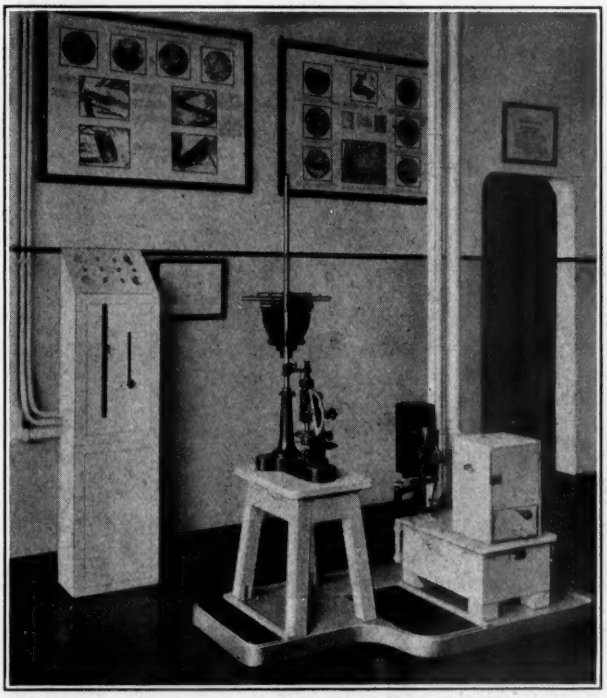


FIGURE 1. VIEW OF ULTRAVIOLET MICROSCOPE

The author is indebted to A. R. Kemp of these laboratories for suggesting the microscopical studies here reported. In his paper Kemp gives chemical analyses of the two latices used in this investigation, and their composition and structure are discussed.

Advantages of the ultraviolet microscope are (*a*) an enormous increase in potential resolving power (about 250,000 lines per inch for the ultraviolet microscope against 140,000 lines per inch for a homogeneous immersion objective of N. A. 1.40); (*b*) selective absorption of the ultraviolet light by many substances; and (*c*) the ability to section optically very small objects which transmit ultraviolet light sufficiently for the purpose.

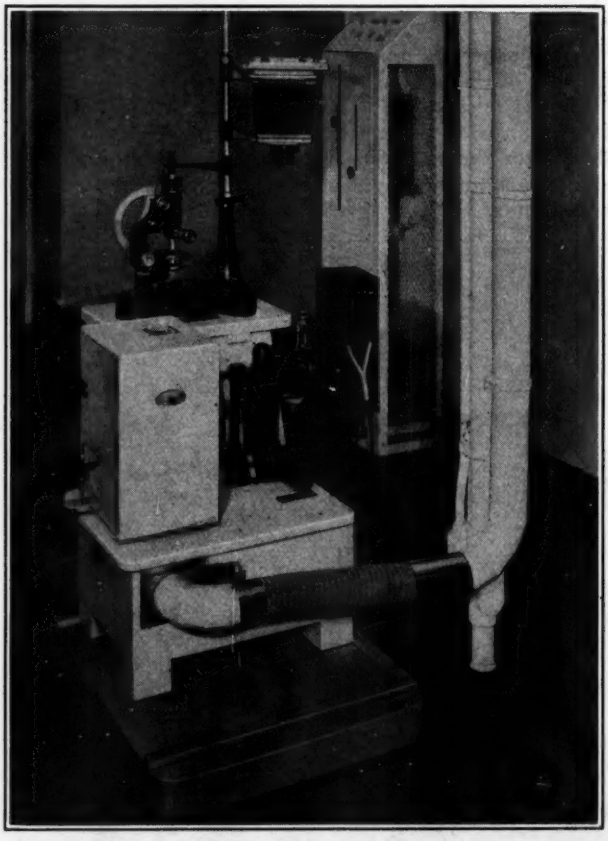


FIGURE 2. VIEW OF ULTRAVIOLET MICROSCOPE SHOWING LIGHT SOURCES, OPTICAL SYSTEM, FUME HOOD, AND EXHAUST.

Brief description of the ultraviolet microscope and methods of optical sectioning are given. Further details will be found in the literature (*2*).

Ultraviolet Microscope

The ultraviolet microscope consists of a monochromator for providing a source of monochromatic ultraviolet light, a

conventional type microscope stand, a fluorescent ocular for viewing the image, and a camera with a sliding plate holder for making serial exposures. The microscope stand and its slow motion are fitted with a device which facilitates optical sectioning. All optical parts are of quartz since optical glass is opaque to light of short wave length. The system is designed to operate on Cd line λ 2750 Å. but may be used about equally well on certain other lines, notably Cd λ 2573 Å. As employed in this investigation, it was not used as a dark field or ultramicroscope but as a transmitted light system yielding real images.

The source of light in the monochromator is a spark gap with cadmium electrodes. Alternating current at 220 volts is stepped up to 10,000 volts by means of a high-tension transformer. Suitable condensers bridge the gap to intensify the spark. Two views of the ultraviolet microscope are shown in Figures 1 and 2 and the optical diagram of the system in Figure 3.

In Figure 1 the power panel is shown against the wall. This panel houses the high-tension transformer and the various switches, meters, and rheostats necessary to control the electrical performance of the apparatus. The microscope and the spark-generating apparatus are mounted on a heavy maple platform supported on sponge rubber.

The monochromator consists, in addition to the spark gap, of the slit, a collimator, two 60° prisms, and a field-of-view diaphragm. The light generated by the spark is spectroscopically decomposed into the characteristic cadmium slit images. These images are not monochromatic but are composite images of groups of lines which the optical train has failed to separate as individuals. The λ 2750 and λ 2573 groups each contain one strong line. The weaker lines in each group do not register an image photographically in the time required to photograph with the strong lines. Consequently for practical purposes each group is monochromatic. Otherwise an image would photograph for each line in the slit image. These images would not be exactly superimposed, and the result of the multiple image would be to defeat the object of using ultraviolet light. Definition and resolution in the image would be ruined.

The microscope and the monochromator are so aligned that the desired wave length enters the base of the microscope support through a window. It is received by a right-angle prism and directed upward to the substage condenser which is focused to illuminate the specimen on the stage above. The specimen is mounted on a quartz slide in a suitable medium and covered with a quartz cover slip.

The specimen is first visually focused with green light obtained from an independent source. A small mirror is swung against the face of the prism adjoining the diaphragm. Light from a mercury vapor lamp is reflected from this

mirror into the microscope. Green light is secured by means of a filter solution placed in a spherical condenser associated with the mercury vapor lamp. After the image is focused visually and the light centered, the searcher eyepiece is swung into position over the ocular and the visible light is replaced by the monochromatic ultraviolet light. The fluorescent image is then focused by the searcher eyepiece and the illumination readjusted for the ultraviolet. When the image is once in focus in the searcher eyepiece, it will also be in focus approximately 30 cm. above. The camera is swung into position, and a photograph is taken.

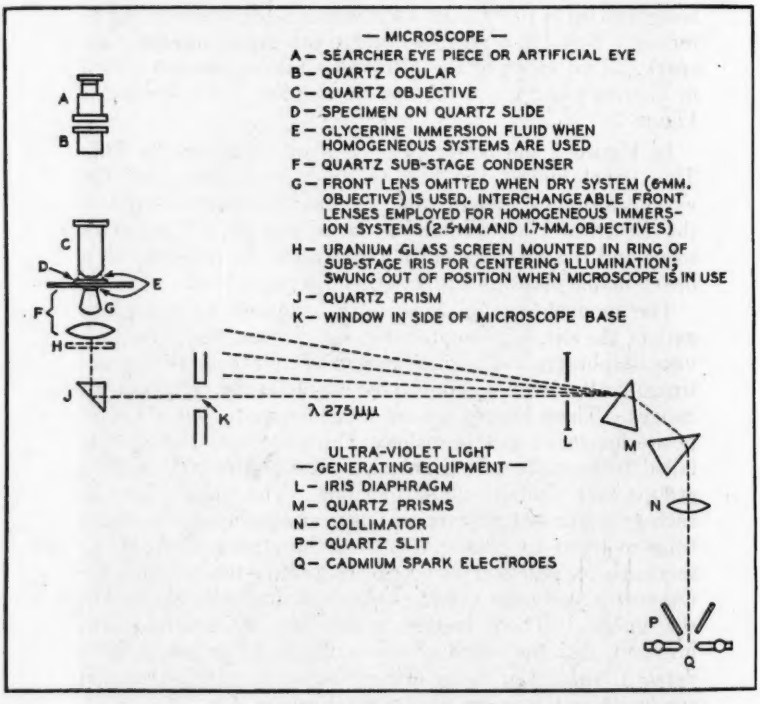

— MICROSCOPE —
A— SEARCHER EYE PIECE OR ARTIFICIAL EYE
B— QUARTZ OCULAR
C— QUARTZ OBJECTIVE
D— SPECIMEN ON QUARTZ SLIDE
E— GLYCERINE IMMERSION FLUID WHEN HOMOGENEOUS SYSTEMS ARE USED
F— QUARTZ SUB-STAGE CONDENSER
G— FRONT LENS OMITTED WHEN DRY SYSTEM (6 MM. OBJECTIVE) IS USED. INTERCHANGEABLE FRONT LENSES EMPLOYED FOR HOMOGENEOUS IMMERSION SYSTEMS (2.5 MM. AND 1.7 MM. OBJECTIVES)
H— URANIUM GLASS SCREEN MOUNTED IN RING OF SUB-STAGE IRIS FOR CENTERING ILLUMINATION; SWUNG OUT OF POSITION WHEN MICROSCOPE IS IN USE
J— QUARTZ PRISM
K— WINDOW IN SIDE OF MICROSCOPE BASE
λ 275 μμ
ULTRA-VIOLET LIGHT
— GENERATING EQUIPMENT —
L— IRIS DIAPHRAGM
M— QUARTZ PRISMS
N— COLLIMATOR
P— QUARTZ SLIT
Q— CADMIUM SPARK ELECTRODES

FIGURE 3. OPTICAL DIAGRAM OF ULTRAVIOLET MICROSCOPE SYSTEM

Depth of focus with the ultraviolet microscope is inappreciable, and for practical purposes the plane of focus may be likened to a geometrical plane. A suitable small object, itself microscopic in size, may be photographed at high magnifications on successive planes. These planes may be spaced 0.25 micron apart and a photograph taken of the details of structure as they appear on each plane. Detail above or below the focal plane does not interfere or appear in the photograph. This is called "optical sectioning."

Optical sections are taken by changing the position of the slow motion of the microscope by small increments, usually 0.25 micron. A pointer (Figure 1) is attached to the slow-motion screw, and a scale with slider properly graduated and calibrated is attached to the microscope stand. The pointer acts as a lever arm and facilitates small changes in focal adjustment.

When small particles are suspended in a liquid the spacing of optical planes cannot be relied upon. Slight changes

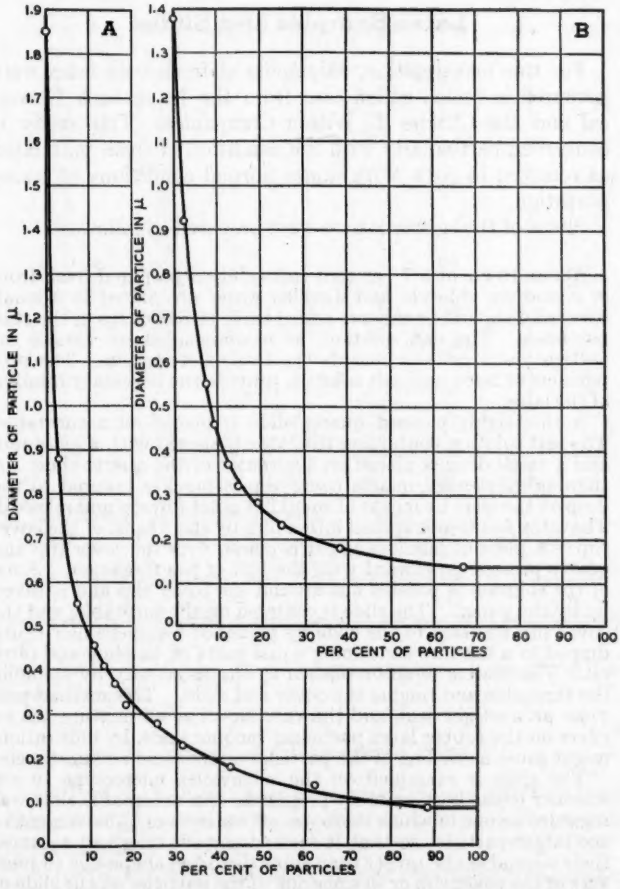


FIGURE 4. PARTICLE SIZE DATA FOR NAUGATUCK LATEX (*A*) AND WILSON LATEX (*B*)

in pressure on the cover slip due to upward or downward movement of the objective may cause a movement of the particles.

Light of short wave length is injurious to the skin. Pre-

cautions are taken by shielding the spark gap with a hood. A forced ventilating system removes the fumes from the hood, otherwise the efficiency of the spark generating apparatus is lowered through the absorption of ultraviolet light by the atmosphere within the hood.

The ultraviolet microscope is strictly a photographic system. The image as seen in the searcher eyepiece is too small and too faintly visible to be of value other than as a means of preliminary focus.

Latex Samples and Slides

For this investigation, shipments of fresh bulk latex were procured in sealed gallon cans from the Naugatuck Chemical and the Charles T. Wilson Companies. This study is concerned particularly with the condition of fresh bulk latex as received in New York under normal conditions of transportation.

Slides of the rubber latices were prepared as follows:

About 10 cc. of a 7 per cent salt solution prepared fresh from C. P. sodium chloride and distilled water are placed in a small covered dish, and to this are added three to five drops of the rubber latex. The salt solution, as recommended by various investigators, arrests or retards the Brownian motion. The proportions of latex and salt solution provide the necessary dilution of the latex.

A thoroughly cleaned quartz slide is placed on a turntable. The salt solution containing the latex is stirred with a glass rod, and a small drop is placed on the center of the quartz slide. A thoroughly cleaned quartz cover slip is quickly lowered to the drop on the slide by means of small flat point forceps and released. The latex solution is spread into a film by the weight of the cover slip. A piece of bibulous paper is placed over the cover slip and gently pressed downward with the ball of the forefinger. Some of the solution is pressed out around the cover slip and is taken up by the paper. The slide is centered on the turntable, and the cover slip is sealed to the slide by means of a camel's hair brush dipped in a mixture containing equal parts of vaseline and olive oil. The sealing is accomplished in the usual way by spinning the turntable and ringing the cover and slide. This method provides an air-tight seal, and the vaseline–olive oil mixture has no effect on the rubber latex particles; lacquer seals, by infiltration, might cause a swelling of the particles under some circumstances.

The slide is examined on the ultraviolet microscope to see whether it has been suitably prepared. An acceptable slide was regarded as one in which there was some freedom of movement to the larger particles so that it seemed certain they had assumed their normal shape rather than some distorted shape due to pressure of the cover slip or to smearing of the particles on the slide or cover. Slide preparations which did not fulfill these considerations were rejected. Immediately after preparation of the slide, the small particles and many of those intermediate between the small and the large particles were observed to be in Brownian motion. In the course of a few minutes this action usually subsided in all except a few of the very small particles. A properly made slide showed no discernible change throughout the course of several hours, other than those indicated in the illustrations given here.

The actual photography of the slide by means of the ultraviolet microscope presents some difficulties. The particles are practically transparent to ultraviolet light of wave length Cd λ 2750 Å. but slightly less so to wave length Cd λ 2573 Å. Because of the slightly improved absorption of

TABLE I. PARTICLE SIZE MEASUREMENTS OF NAUGATUCK RUBBER LATEX (40.02 PER CENT SOLIDS)

A, Diam. at Measuring Screen *Mm.*	Actual Diam. *Microns*	No. Particles P-2315	P-2316	P-2319	P-2320	*D*, Total No. Particles	Product, $A \times D$
40	1.85	..	..	..	1	1	40
30	1.38	..	..	1	3	4	120
26	1.20	..	..	..	1	1	26
25	1.15	2	..	2	1	5	125
24	1.11	..	..	..	1	1	24
23	1.06	1	..	..	..	1	23
22	1.02	..	1	1	..	2	44
20	0.92	2	5	2	2	11	220
19	0.88	..	1	..	..	1	19
18	0.83	1	..	..	..	1	18
17	0.78	3	5	1	..	9	153
16	0.74	2	2	1	..	5	80
15	0.69	..	8	4	3	15	225
14	0.64	8	1	..	1	10	140
13	0.60	1	1	..	..	2	26
12	0.55	9	13	5	6	33	396
11	0.51	4	2	..	1	7	77
10	0.46	7	10	3	4	24	240
9	0.41	10	5	5	4	24	216
8	0.37	6	10	5	7	28	224
7	0.32	15	19	22	18	74	518
6	0.28	13	19	16	14	62	372
5	0.23	32	29	25	27	113	565
4	0.18	55	46	41	57	199	796
3	0.14	78	72	53	68	271	813
2	0.09	8	38	42	28	116	232
Total	..	257	287	229	247	1020	5732

Magnification at measuring screen, × 21,600

Diam. of av. particle at measuring screen = $\frac{5732}{1020}$ = 5.61 mm.

Actual diam. of av. particle = $\frac{5.61}{21,600}$ = 0.00026 mm. = 0.26 micron

light at 2573 Å., this wave length was used throughout the investigation.

Particle Shape and Size

A study of the ultraviolet photomicrographs resulting from this investigation shows the predominant shape of the particle to be spherical.

A few of the larger particles appear pear-shaped or elongated. Certain of these nonspherical particles seem to be homogeneous throughout and are apparently single particles. Others are irregular in shape because two or more particles have joined but not merged.

Mathematical analysis of particle-size data indicates that only about 10 per cent of the particles in the latices studied are larger than 0.50 micron.

The method of particle size measurement employed is one commonly used with minor modifications to determine particle size of pigments. The ultraviolet plate is contact-printed to obtain a transparency on glass suitable for lantern slide projection. This transparency is projected to a white screen, cross-ruled into 2-inch (5-cm.) squares. From the center of the field as projected on the screen a given group of cross rulings is selected, and the diameter of every particle is measured to the nearest millimeter. Magnifications are carefully calibrated to avoid errors.

TABLE II. PARTICLE SIZE MEASUREMENTS OF WILSON RUBBER LATEX (40.60 PER CENT SOLIDS)

A, Diam. at Measuring Screen	Actual Diam.	No. Particles					*D*, Total No. Particles	Product, *A* × *D*
		P-2338	P-2339	P-2341-B	P-2342	P-2343		
Mm.	*Microns*							
30	1.38	..	..	1	..	2	3	90
28	1.29	1	..	1	..	..	2	56
25	1.15	2	..	1	4	2	9	225
24	1.11	..	..	..	1	..	1	24
23	1.06	..	..	..	3	2	5	115
22	1.02	2	1	..	..	2	5	110
20	0.92	3	3	2	8	5	21	420
18	0.83	2	2	2	1	2	9	162
17	0.78	..	1	..	..	..	1	17
16	0.74	..	1	..	..	..	1	16
15	0.69	5	7	5	4	8	29	435
14	0.64	..	..	1	1	..	2	28
12	0.55	7	2	5	9	2	25	300
11	0.51	3	..	..	..	..	3	33
10	0.46	7	4	5	4	11	31	310
9	0.41	2	..	..	..	..	2	18
8	0.37	6	3	4	6	3	22	176
7	0.32	17	5	13	11	8	54	378
6	0.28	24	4	8	18	10	64	384
5	0.23	26	18	29	32	55	160	800
4	0.18	75	40	59	65	102	341	1364
3	0.14	86	54	89	88	77	394	1182
Total	..	268	145	225	255	291	1184	6643

Magnification at measuring screen, × 21,600

Diam. of av. particle at measuring screen = $\frac{6643}{1184}$ = 5.61 mm.

Actual diam. of av. particle = $\frac{5.61}{21,600}$ = 0.00026 mm. = 0.26 micron

In this work all latex particles have been measured as spherical particles, although a certain few of the particles were not spherical and an approximation was made in their measurement. The number of such particles was too few to have significant effect. Particle size data for the two latices studied are given in Tables I and II, and are plotted in Figure 4 to show percentage of particles distributed on a basis of the diameter of the particles in microns.

The two commerical latices from entirely different sources yield practically identical results. The diameter of the average particle for each is 0.26 micron. The maximum size particle is about 2 microns, and the minimum size about 0.09 micron. The particle size distribution for the two latices is slightly different.

These results are not in agreement with the published data of other investigators. The methods described here have resulted in a multitude of small particles being resolved and measured which perhaps had not heretofore been clearly disclosed by microscopic investigation. As a result, the diameter of the average particle and the diameter of the minimum size particle are much smaller.

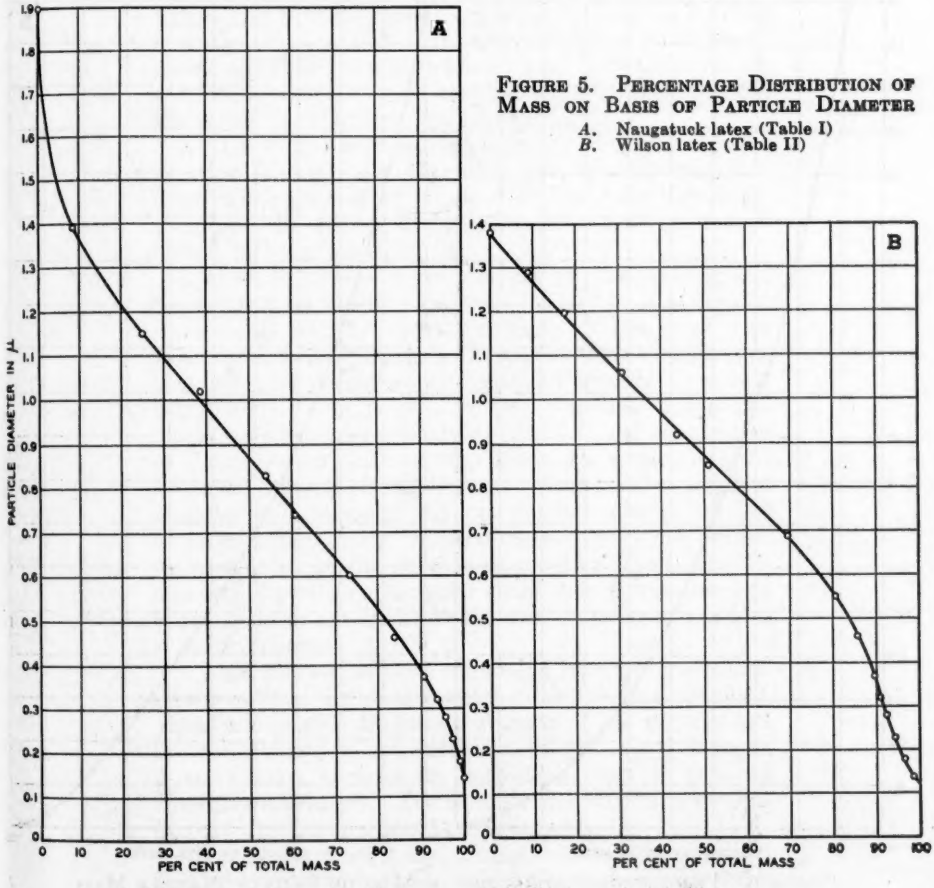


FIGURE 5. PERCENTAGE DISTRIBUTION OF MASS ON BASIS OF PARTICLE DIAMETER
A. Naugatuck latex (Table I)
B. Wilson latex (Table II)

It is not known whether all particles in the latex have been resolved and accounted for. In the tables the maximum number of particles occurs at a diameter of 3 mm. at the measuring screen. Table I shows a falling off in the number of particles at a diameter of 2 mm.; in Table II, 3 mm. is the minimum diameter recorded. Greater resolving power, higher magnifications, and more precise methods of measurements may reveal a gradual tapering off in particle size with a larger number of small particles resolved.

The data of Tables I and II were calculated by R. L. Dietzold, research mathematician of these laboratories, to show the distribution of particles on a mass basis; his results are given in Figures 5 and 6. These graphs show that, although approximately 92 per cent of the particles is 0.50 micron or less in diameter, only about 18 per cent of the mass is confined to

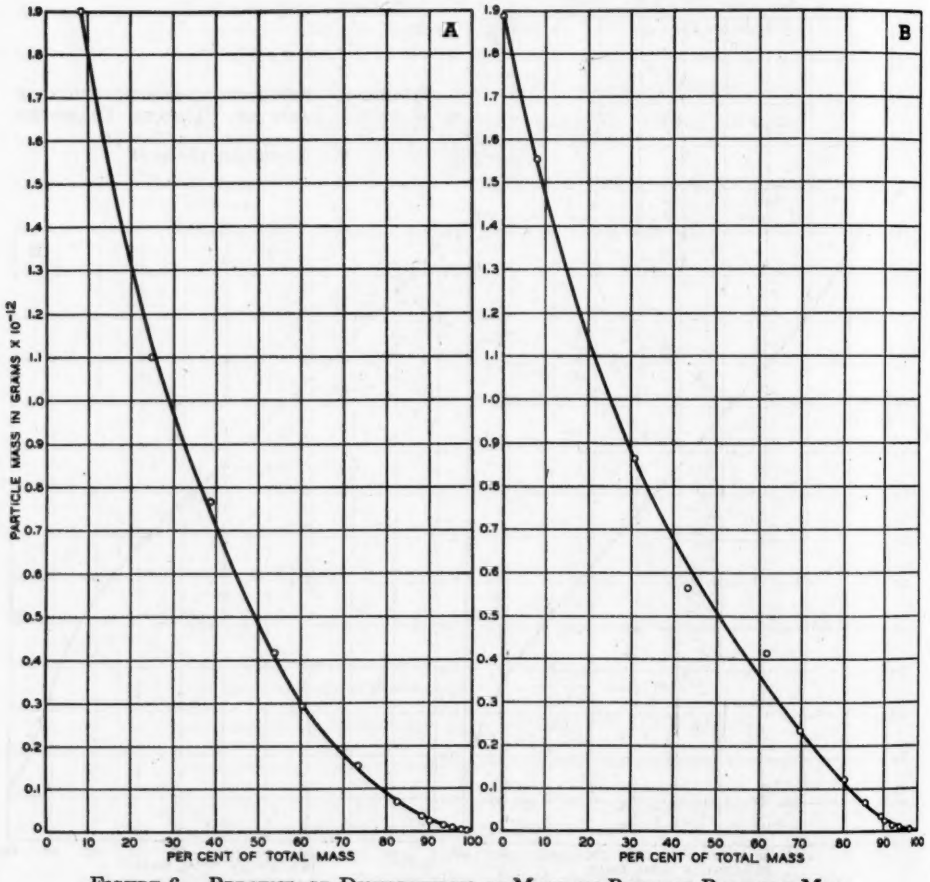


FIGURE 6. PERCENTAGE DISTRIBUTION OF MASS ON BASIS OF PARTICLE MASS

A. Naugatuck latex (Table I)
B. Wilson latex (Table II)

this size range. For each latex, 50 per cent of the total is in particles less than 0.50×10^{-12} gram in mass or less than 0.89 micron in diameter.

The calculated average particle mass for the Naugatuck latex (Table I) is 0.054×10^{-12} gram, and for the Wilson latex (Table II), 0.053×10^{-12} gram.

Discussion

A representative group of ultraviolet photomicrographs of the two latices is given in Figures 7, 8, and 9; the wave length used was 2573 Å. at a magnification of 1800 diameters. Certain general observations may be made on Figures 7, 8, and 9:

1. Instantaneous photographs were not possible with the ultraviolet microscope. A minimum time of 10 seconds was required for correct exposure. During this interval the light from any small particle in Brownian motion would be scattered and diffused so that an image on the plate would not result. The number of such particles in a given field was too few to have any significant effect on the total.

2. The rubber latex particle is known to have a negative electrical charge. All the ultraviolet photomicrographs show that certain of the smaller particles have apparently given up their charges, and these particles have become attached to larger particles.

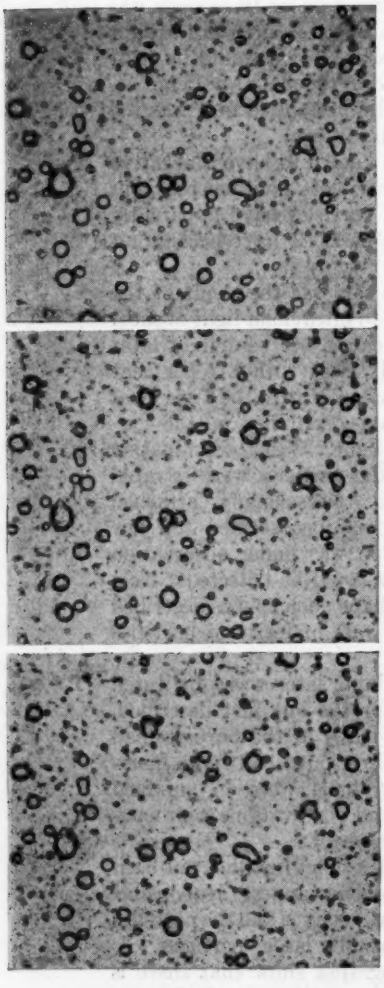
A question arose as to whether this was the result of the salt solution or whether exposure to ultraviolet light of short wave length may have been the cause. A sample of latex was prepared by diluting the bulk latex with 0.75 per cent ammonium hydroxide in water instead of with the 7 per cent salt solution. This preparation was examined on the cardioid ultramicroscope with visible light. Visual examination of the dispersion disclosed that the particles were in rapid Brownian motion as individuals. Occasionally, attached particles were observed but the number seemed too few to be important. The preparation was under observation for several hours, and no changes could be detected. Now and then a particle of irregular shape such as was described above could be detected, but the vast majority of particles appeared spherical.

A 7 per cent salt solution containing latex was substituted on the cardioid ultramicroscope for the one just described. Visual examination disclosed that many of the particles had become attached to one another in groups of two or more. A great many particles as individuals were in subdued Brownian movement. The cardioid observations were confirmed by instantaneous photomicrographs.

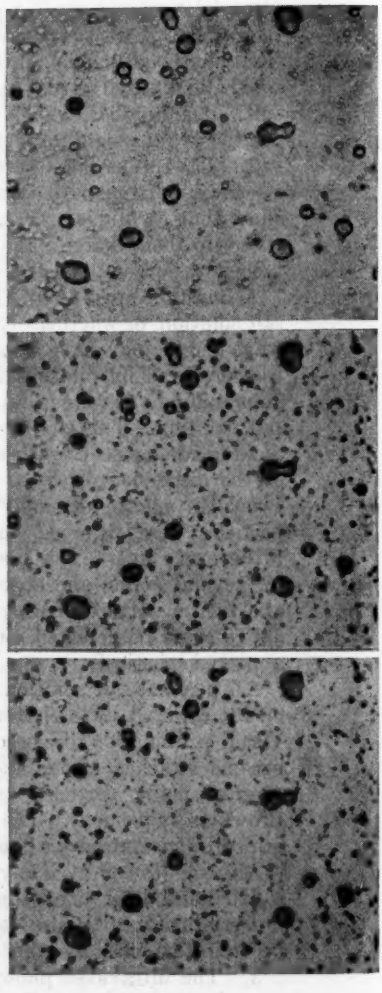
Although the effect, if any, of ultraviolet light has not been isolated and determined, the salt solution appears responsible for certain of the particles losing their charges and the particles becoming attached to other and usually larger particles.

3. The ultraviolet photomicrographs show that there is a tendency for the smaller particles to form in straight or slightly curved lines. Sometimes there appears to be a gradation in the sizes of the particles forming the line—a large particle at one end and a gradual diminution in particle size towards the other end. In some cases this regularity in gradation of particle sizes does not hold. The particles are usually not in contact but are often quite evenly spaced.

The large particles do not appear similarly arranged in lines. This may be due solely to the fact that the dilution of the latex has resulted in few large particles being present in a field and thus the effect is obscured. Other investigators have reported a straight-line arrangement of the particles. Their observations probably refer to the large particles.



P-2315. Optical sections spaced 0.25 micron

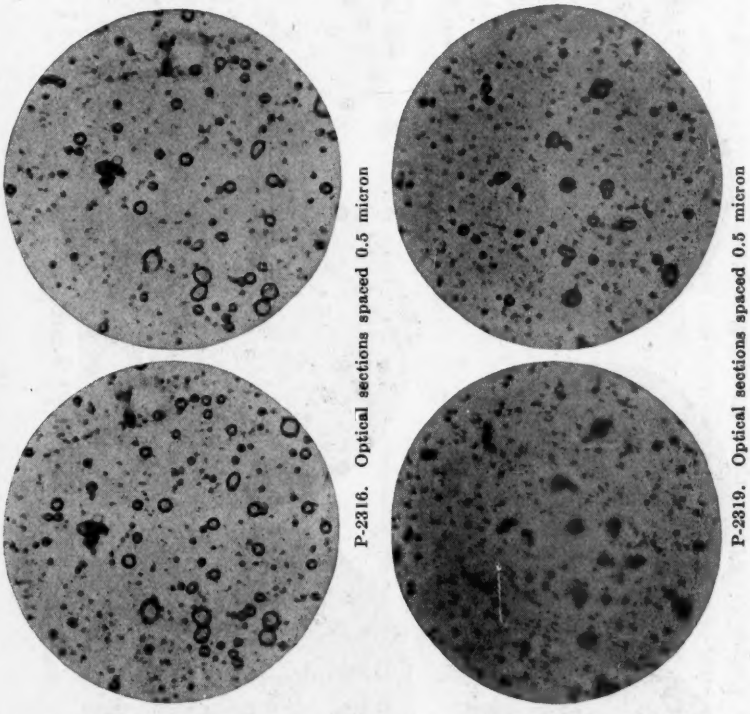


P-2320. Optical sections spaced 0.25 micron

The alignment of the smaller particles is too common to be accidental. Whether it is due to some electrical effect or to some other cause has not yet been established.

4. The ultraviolet photomicrograph of an optical plane through a typical latex particle shows a dark boundary circle. Inside this circle structural detail is not revealed. The con-

tents of the latex particle as viewed by the ultraviolet microscope appears to be a homogeneous substance practically transparent to ultraviolet light of λ 2573. The dark circle may indicate absorption of the ultraviolet light. If this interpretation is correct, the chemical composition at the surface of the latex particle must be different from the contents to account



P-2316. Optical sections spaced 0.5 micron

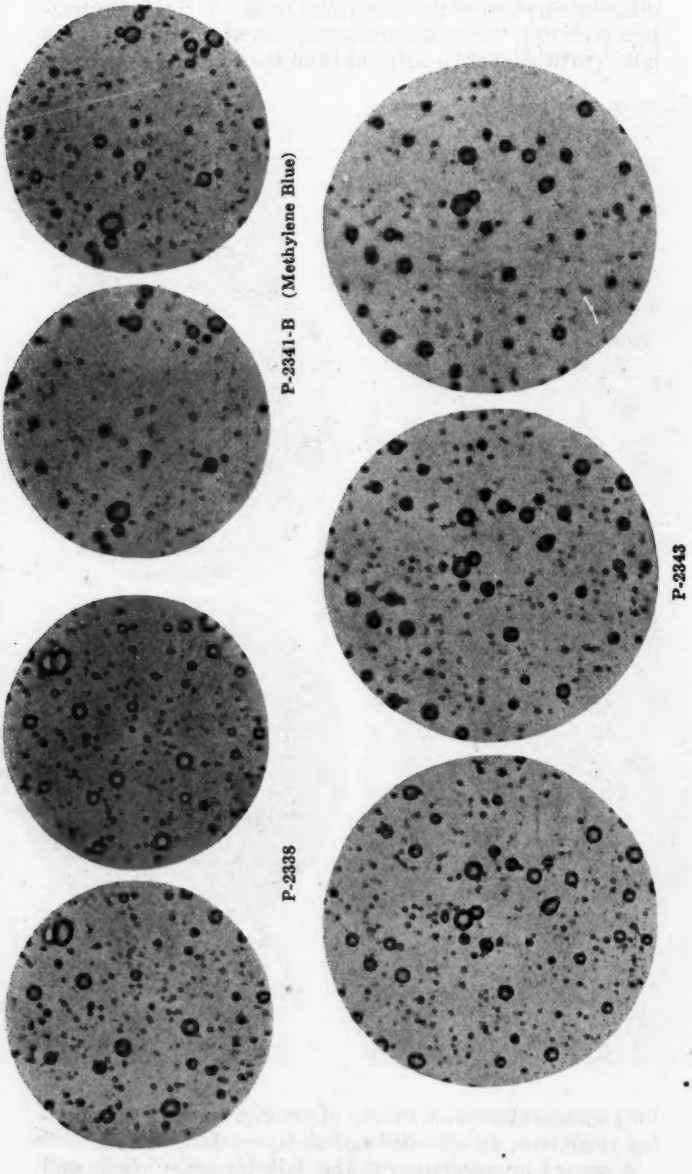
P-2319. Optical sections spaced 0.5 micron

FIGURE 7. NAUGATUCK LATEX

for a surface absorption effect. This might mean a surrounding membrane, an adsorbed surface layer effect, or both.

A second interpretation of the dark boundary circle, and perhaps one with which many will agree, is that the light (either visible or ultraviolet) is reflected and refracted from or by the surfaces of the particles, and therefore the particles

become visible. In the searcher eyepiece of the ultraviolet microscope it is almost impossible to see the particles so that

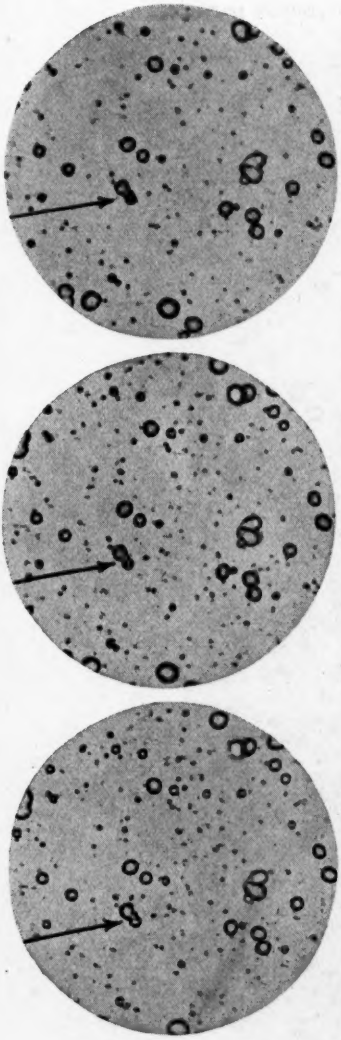


the refractive index of the dispersing medium and of the particle at λ 2573 must be nearly the same.

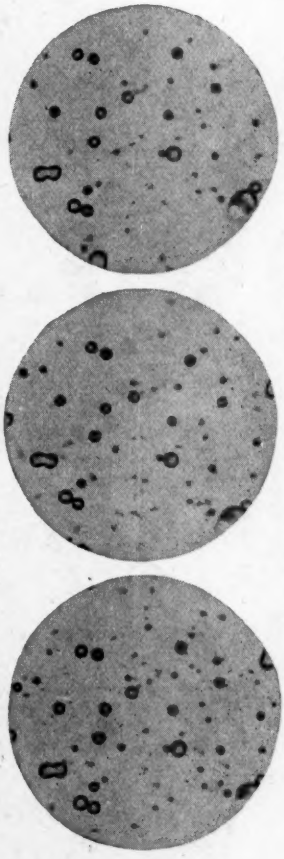
The evidence one way or the other on the nature of the sur-

face is not conclusive. Further investigation will be required.

5. When two fresh samples of bulk rubber latex are investigated by the methods described, almost identical particle



P-2342. An irregular-shaped particle appearing in the left-hand section is clearly resolved into three particles on the right.



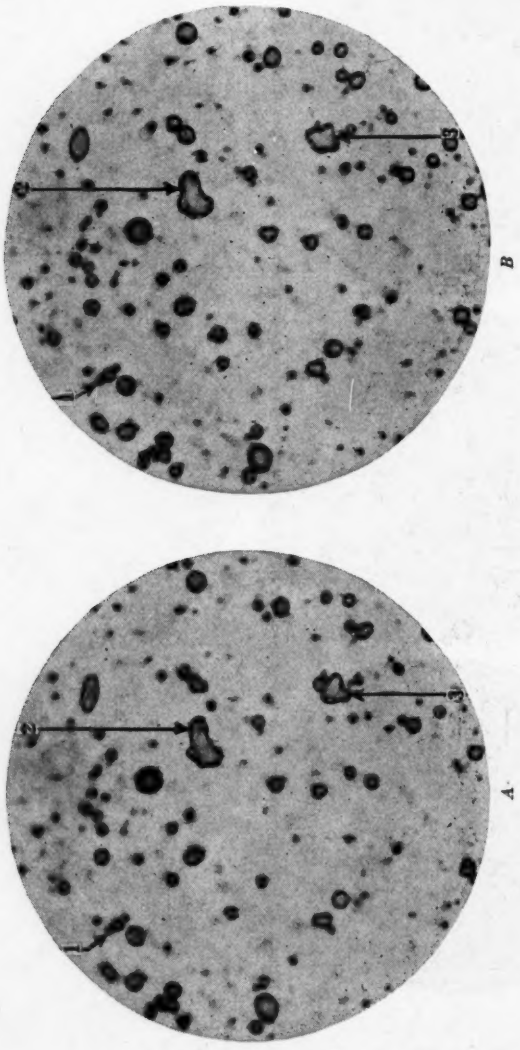
P-2339. One elongated particle appears to have been formed by the union of two particles.

FIGURE 8. WILSON LATEX, OPTICAL SECTIONS SPACED 0.25 MICRON APART

size data result. The diameter of the average particle in each case is computed as 0.26 micron, the diameter of the maximum particle is about 2.0 microns, and the diameter of the minimum particle is about 0.09 micron. In either case

about 90 per cent of the particles is 0.5 micron or less in diameter.

6. The predominant shape of the latex particle appears to be spherical. When a particle is irregular in shape, optical sections usually, but not always, disclose that such a particle has been formed from two or more smaller particles.



7. There is some indication that egg-shaped particles may develop through the merging of two or more particles (Figure 9). Further investigation is required to establish the soundness of this conclusion.

The plates of Figure 9 were taken about 5 weeks after those shown in Figure 7 plate P-2315. In the meantime the sample of latex in a glass-stoppered bottle was kept in a refrigerator maintained at approximately 6° C. The sample was not shaken, and creaming had taken place. On several occasions the bottle was exposed to moderate atmospheric conditions for 3 to 5 hours.

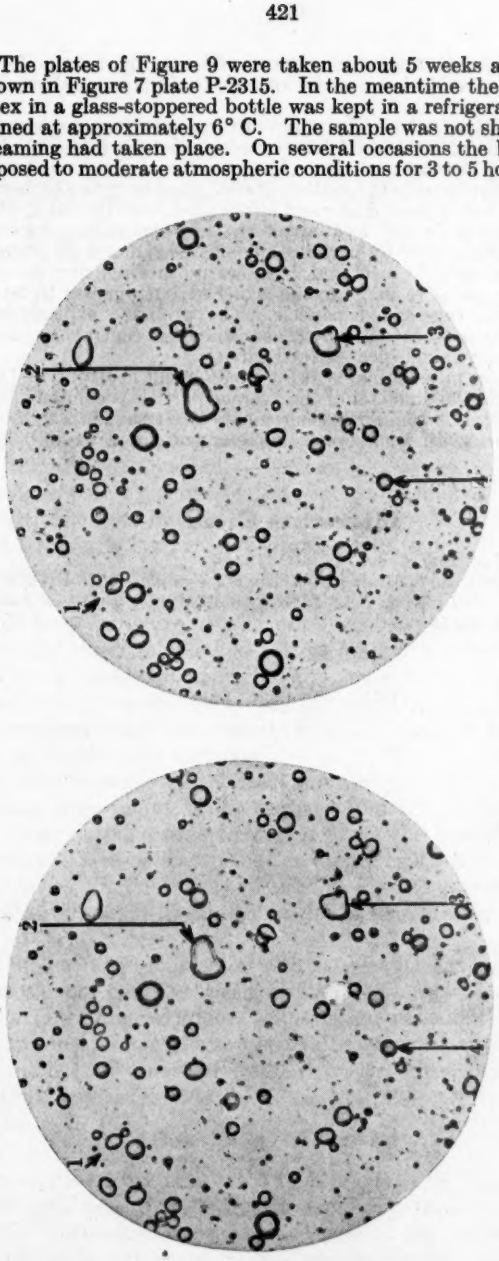


FIGURE 9. WILSON LATEX

P-2347; optical sections spaced 0.25 micron apart

Each plate represents an optical spacing of approximately 0.25 micron. *A* and *B* were taken in quick succession soon after the slide was made. While *A* and *B* were being developed, about 15 minutes elapsed. The aperture of the illuminating beam was reduced somewhat, and plates *C* and *D* were then taken in quick succession.

Particles 2 and 3 are agglomerates of several particles. Particle 4 has moved from a near-by location to the position shown in *C* and *D*.

At position 1 (*A* and *B*) a group of three spherical particles is shown in chain formation. The center particle is larger in diameter than the end particles. In plates *C* and *D* the small end particle to the upper left has disappeared, and the central spherical particle has become larger and egg-shaped, with the small end pointing to the former location of the missing small spherical particle. Other near-by particles remain the same in all plates. The central particle in *C* and *D* shows no internal division as though two particles had become attached but appears to be a homogeneous egg-shaped particle. The probable explanation seems to be that the small particle and the large central one have united to form a single pear-shaped particle.

Particle size measurements of Figure 9*B* result in a total of 143 particles, and the diameter of the average particle is computed to be 0.608 micron. Similar measurements of *C* result in a total of 509 particles, with an average diameter computed to be 0.368 micron.

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(1) Green, *Ind. Eng. Chem.*, **17**, 802 (1925).
(2) Lucas, Am. Inst. Mining Met. Engrs., *Pamphlet* **1576-E** (1926); *Proc. Natl. Acad. Sci.*, **16**, Sept., 1930; *J. Franklin Inst.*, **217**, June, 1934.

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Purification and Concentration of Rubber Latex, with Special Reference to Dialysis

H. P. Stevens, J. W. W. Dyer, and J. W. Rowe

London, England

There are three manufacturing processes in use for the concentration of latex, two of which also give some purification. Evaporation by heating with a potash soap stabilizer added[1] gives a reversible paste of 60–70 per cent concentration, containing all the serum components. Centrifugal concentration[2] to 60 per cent gives a mobile fluid, partly purified by the removal of some of the serum. Creaming[3] gives a partly purified fluid latex, containing, however, the creaming agent. It is also possible to purify latex by some form of filtration,[4] either through a porous filtering medium or by some type of ultra-filter. So far as is known, however, this process has not found practical application.

Articles made from latex are usually obtained by evaporation, coagulation, or gelling, and contain water-soluble and hygroscopic substances which occur in the serum and in many cases are undesirable components of the finished product. This paper describes results obtained in the investigation of dialysis as a method of removing these water-soluble components from latex, and in the concentration of dialyzed latex by evaporative methods.

Dialysis has been regarded as the least promising of the various possible purification processes, on account of its slowness and the probability of the latex putrefying and coagulating during treatment under the tropical conditions on the estates. However, it will be shown that an 80 per cent purified latex may be obtained in eight hours, ammonia may be used as a preservative, and tropical temperatures are if anything an advantage, a rise of temperature increasing the rate of dialysis.

Commercial dialyzers are built up of alternate water and liquor cells, separated by sheets of parchment paper, so designed as to give a large surface for diffusion for a relatively small volume of liquor. This design was adopted for use with latex. Ammonia at the considerable dilution generally used in preserved latex has little or no chemical action on the paper, and there is little danger of rupturing the septum from this cause.

Description of Dialyzer

The dialyzer unit is built up of teak frames about 21 inches square and $1/2$ inch thick, separated by sheets of the dialyzing membrane to form alternate latex and water cells. The membranes are supported against the imposed air pressure by stainless steel wire grids, supported by teak spacing blocks in the water cells. The whole is clamped between iron frames bolted together. These are the essential parts of the dialyzer itself, apart from accessory apparatus. The assembly into the simplest unit is shown diagrammatically in Fig. 1, with the parts spaced for clearness. The cells are provided with inlet and outlet connections. The dialyzer is mounted vertically on a table, with a water heater tank and circulating pump

below (Fig. 2). To get consistent results it is important to maintain a uniform flow through the water cells, and this is obtained by feeding the water into the bottom of the cells from a constant head, the overflow returning to the heater tank.

The level of latex in the cells is read on gage glasses. The bottoms of the cells are joined together. When two units are employed, the latex cells in each are connected separately to two air lines which are maintained at different pressures. By an arrangement of coupled taps the connections to the two different pressures may be reversed at will. Further details may be obtained by reference to British Patent 458,130.

Methods of Operation

(*a*) *With To-and-Fro Movement of the Latex.*—This is the best method to use for the rapid dialysis of latex. The cells are half filled with latex and connected to the two air lines at different pressures. The water circulation is started and the temperature adjusted. The latex flows from the unit connected to the higher pressure to the other unit. The air connections are then reversed and the latex flows back again. By this device the latex is continually mixed, which accelerates dialysis, and is maintained under a pressure which counteracts the dilution of the latex which would otherwise occur, due to the osmotic activity of the water-soluble components of the latex serum.

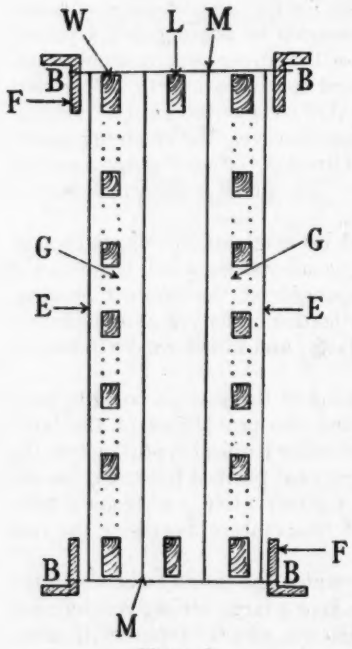

Figure 1

F, frame; B, bolts; E, end plate; G, wire grids; W, water cell; M, dialyzing membrane; L, latex cell

(*b*) *With Stationary Latex.*—This arrangement does not give such rapid dialysis, but can be more accurately standardized. One latex cell only is used. The water circulation is as before.

Results Obtained in the Dialysis of Latex

(*a*) *With To-and-Fro Movement of the Latex.*—Using the dialyzer as described above with four latex cells in each unit, about 14 liters of normal ammonia-preserved latex may be purified of 80–85 per cent of its diffusible impurities in 8–9 hours, using two charges of soft water at 55°. Substantially all the remaining impurities can be removed by a further similar treatment. Best results are obtained when the air pressures are adjusted so as to allow about 15 per cent dilution.

On dismantling the dialyzer, it is found that all the latex does not drain out. A proportion adheres to the membranes as a paste of about 70 per cent dry rubber content. This paste consists of uncoagulated latex and, although very unstable to mechanical treatment, it can with care be redispersed in a dilute solution of ammonia to an apparently normal latex. It does not, however, redisperse in the purified latex under the mixing effect of the to-and-fro movement.

When allowing a dilution of about 15 per cent to occur, the formation of paste is slight. However, on raising the air pressure so as to keep the latex at constant

volume, the formation of paste on the papers becomes considerable. This paste formation is objectionable for two reasons: firstly, because it partly blocks the dialyzing membrane and retards purification, and secondly, because the loss of this more concentrated portion from the bulk of the latex reduces the dry rubber content of the liquid product. In spite of various modifications in procedure, the only known way of preventing the paste forming was to allow dilution. This is not desirable, since the demand is for concentrated latices. The inclusion of a small proportion of stabilizer, *e. g.*, 1 per cent of Lissapol A, in the latex reduces the paste formation considerably, but does not prevent it sufficiently.

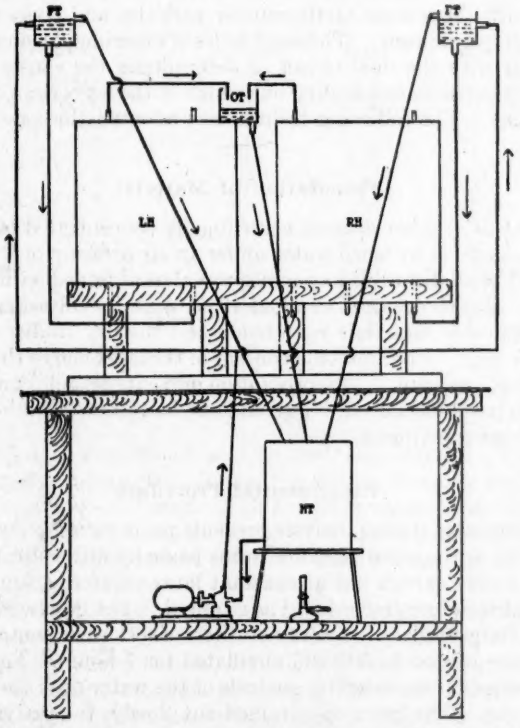

Figure 2—Dialyzing Plant, Showing Water Circulation
FT, feed tanks; OT, overflow tank; LH, RH, dialyzer units; HT, heater tank

There are no references to this phenomenon in the literature, so the following series of experiments was made in an attempt to understand the causes of paste formation, as a preliminary to preventing it.

(*b*) *With Stationary Latex.*—The experiments were carried out with stationary latex in one cell, thus giving more accurate control of conditions.

Before starting the main series of experiments, some preliminary trials were made. Some normal ammonia-preserved latex was completely purified by dialysis of all diffusible impurities. On further treatment in the dialyzer under no external pressure, the volume remained constant, and, as would be expected, no paste was formed on the papers. When an air pressure equal to 7 inches of mercury

was applied, the volume diminished, due to ultra-filtration, and a layer of paste was formed on the membrane. All further experiments were, therefore, carried out at constant volume, so as to prevent the ultra-filtration effect. Constancy of volume of the latex is obtained by adjusting the air pressure during the progress of dialysis so as to balance the osmotic effect of the diffusible impurities in the latex.

Some normal, ammonia-preserved latex was now dialyzed under constant-volume conditions, and considerable deposit of paste was found on the membranes. This cannot be due to ultra-filtration, since there has been no concentration. It can be due only to the removal by dialysis of the diffusible impurities. By some means the water-soluble components of the latex, as they diffuse to and through the membrane, carry with them some of the rubber particles and concentrate them in a pasty layer on the membrane. The main series of experiments, now to be described, was carried out with the dual object of determining the causes of this hitherto unrecorded phenomenon, and finding out which of the latex components was likely to be responsible. The following technic was adopted throughout this series of experiments.

Preparation of Material

A 60 per cent dry rubber content centrifugally concentrated latex was dialyzed with several changes of softened water under an air pressure of 1 inch of mercury. A latex purified of all diffusible impurities was thus obtained without loss by paste formation, and dilution occurred to about 45 per cent dry rubber content. Various additions of diffusible materials were made and the dry rubber content was adjusted to 40 per cent. The ammonia content of the latex and of the dialyzing water was adjusted to 0.1 per cent. This precaution prevents coagulation of the latex. It has no effect on paste formation. Two and one-half liters of the compounded latex were used in each experiment.

Experimental Procedure

Dilution of the latex during dialysis prevents paste forming; concentration of a purified latex by an imposed pressure forms paste by ultra-filtration. Therefore, all experiments were carried out at constant latex volume, a suitable air pressure being applied at the start and reduced as required. The latex volume was checked by readings on the gage glass. Twenty-six liters of soft water containing 0.1 per cent of ammonia were heated to 50° and circulated for 7 hours. The weight of each addition diffused was calculated by analysis of the water or of the latex at the end of the experiment. The latex was drained out slowly, the dialyzer stripped, and the membranes with adhering paste were removed, dried, and weighed, the paste being recorded as the weight of rubber which is deposited on the membranes.

Results

The distribution of the paste on the membranes is usually uniform when the flow of water on the other side is uniform, as it is in this series. However, when the addition is sodium chloride, sodium carbonate, or sodium sulfite, the paste is deposited almost entirely on the top half of the membranes. The bottom half of the membranes is clear of paste, except opposite the wires of the stainless steel grids and the teak separating blocks in the water cells, where a little is deposited. This is an unexpected result, since diffusion is presumably least opposite these obstructions, and in all other cases the deposition of paste occurs where most diffusion can occur.

The results for each addition are summarized in Table I. For comparison, the figures for a normal ammonia-preserved latex with its existing diffusible components are given, and those for the addition of "serum solids" which are obtained by the evaporation of the serum remaining after the coagulation of the rubber during the commercial preparation of crepe. The paste deposited per gram of each addition diffused is calculated, and the additions are arranged in this order with the molecular weight of the addition in the last column.

TABLE I

ADDITIONS TO LATEX IN ORDER OF "PASTE PER GRAM DIFFUSED"

Addition Per Cent on Latex	Grams Diffused	Paste	Paste per Gram Diffused	Mol. Wt.
2.5 per cent sodium stearate	0	0	..	306
2.5 per cent sodium sulfite	58	36	0.62	126
3.0 per cent sodium carbonate	56	66	1.2	106
2.5 per cent sodium chloride	53	73	1.4	59
4.6 per cent ammonia[a]	94	160	1.7	35
5.0 per cent borax	65	154	2.4	202
12.0 per cent sucrose	100	250	2.5	342
5.0 per cent sucrose	59	168	2.8	342
6.0 per cent glucose	80	227	2.8	180
2.5 per cent glycerol	55	178	3.2	75
2.5 per cent urea	47	164	3.5	60
3.3 per cent existing	32	111	3.5	...
3.5 per cent serum solids	45	160	3.6	...
1.75 per cent serum solids	26	140	5.4	...
0.5 per cent serum solids	12	88	7.3	...

[a] Calculated as NH_4OH.

Sodium stearate does not diffuse, and no paste was formed. The electrolytes come next, and the "paste per gram diffused" is related inversely to their molecular weight, with the exception of borax. The non-electrolytes form more "paste per gram diffused," which is also related inversely to their molecular weight. The existing water-soluble components of latex and the added serum solids form most "paste per gram diffused."

The "paste per gram diffused" is greater from more dilute solutions of the same material, *e. g.*, 12 per cent sucrose, 2.5; 5 per cent sucrose, 2.8; 3.5 per cent serum solids, 3.6; 1.75 per cent serum solids, 5.4; 0.5 per cent serum solids, 7.3.

This suggests that accurate comparisons should be made between additions at equivalent concentrations, either at equal molecular weight or equivalent weight concentrations or at isotonic concentrations. With the exception of the 5 per cent sucrose and the 1.75 per cent and 0.5 per cent serum solids, the additions give roughly isotonic concentrations. Observations at more accurately isotonic concentrations might show greater regularity.

The "paste per gram diffused" of the various additions is plotted against their molecular weight in Fig. 3. The separation of the electrolytes and the non-electrolytes into two groups with borax occupying an intermediate position is clearly shown. It is interesting to note that the first three electrolytes, sodium sulfite, sodium carbonate, and sodium chloride, are the only three of the substances which cause a non-uniform deposition of paste, with the peculiar reversed effect on the lower half of the dialyzing membranes, which has already been described at the beginning of this section on "Results." No attempt at an explanation of these effects is made at this stage.

The inverse relationship between "paste per gram diffused" and the molecular weight suggests that the "paste per mol. diffused" might show some regularity. These values are shown in order in Table II and compared with the molecular weight in Column 3 and with the estimated average particle weight in Column 4. The average particle weight has been calculated from the degree of electrolytic dissociation at the concentration of the addition at the beginning of the experiment. The degree of electrolytic dissociation has been calculated from the available conductivity data at 18° as sufficient values at 50°, the temperature of the experiments, are not available. Where available they indicate that temperature effects over this range are small. During an experiment the degree of electrolytic dissociation will be increasing as the concentration decreases. However, the concentrations used in the calculations are the initial concentrations in the latex, which have been taken as average values, since the true concentration, *i. e.*, the concentration in the serum, will be higher initially and lower finally than the value taken. The degree of electrolytic dissociation used is shown in Column 5. The value for borax is an assumed one, since sufficient reliable determinations do not seem to be available.

TABLE II

ADDITIONS TO LATEX IN ORDER OF "PASTE PER MOL. DIFFUSED"

Column 1	Column 2	Column 3	Column 4	Column 5
	Paste per Mol. Diffused	Mol. Wt.	Estimated Average Particle Wt.	Estimated Average Degree of Electrolytic Dissociation Per Cent
4.6 per cent aq. NH_3[a]	60	35	35	1
2.5 per cent NaCl	81	59	33	78
2.5 per cent Na_2SO_3	78	126	55	65
3.0 per cent Na_2CO_3	125	106	53	50
2.5 per cent urea	210	60	60	..
2.5 per cent glycerol	242	75	75	..
5.0 per cent borax	480	202	101	50
6.0 per cent glucose	511	180	180	..
12.0 per cent sucrose	855	342	342	..

[a] Calculated as NH_4OH.

The non-electrolytes are in the same order as their molecular weights, but the electrolytes are not, neither do they all come together, borax appearing among the non-electrolytes. However, on comparing the "paste per mol. diffused" with the estimated average particle weight (Table II, Column 4) it is found that the order is very nearly the same. This relationship is shown graphically in Fig. 4. The points do not fall on a smooth curve, but the regularity is sufficiently noticeable, particularly with the non-electrolytes, to say that the "paste per mol. diffused" is directly related to the particle weight: in other words, the paste formed per particle diffusing is approximately proportional to the weight of the particle. This conclusion is tentative only, and may have to be modified by further work which is in hand on this problem.

Discussion

The phenomenon of colloidal concentration at the membrane in constant-volume dialysis, which has been described above, is of interest in a wider field than latex technology. As far as the authors are aware it has not previously been recorded in the literature, and it is anticipated that it will be found to occur with colloids other than latex particles. The living cell in plants and animals is a constant-

volume dialyzer with a semipermeable membrane as cell wall. It contains colloids and crystalloids. When the crystalloids dialyze out, as they do at times, they will concentrate the colloids on the cell wall. This should help to explain the mechanism of growth in thickness of cell walls, as occurs, for example, in the woody tissues of plants. It may also explain the gradual cessation of flow and blocking of the ends of the latex vessels after tapping, the cream deposited on the cell walls being

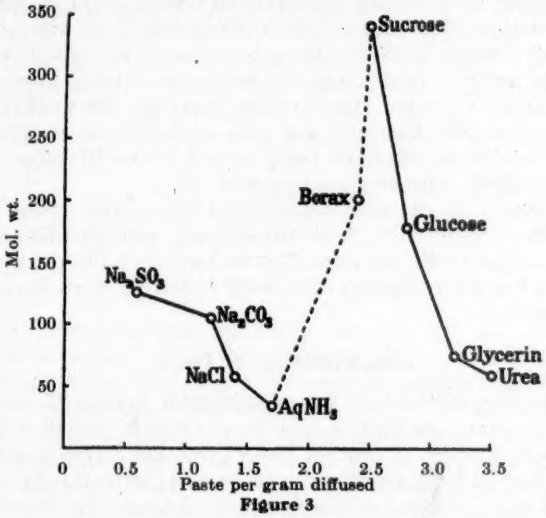

Figure 3

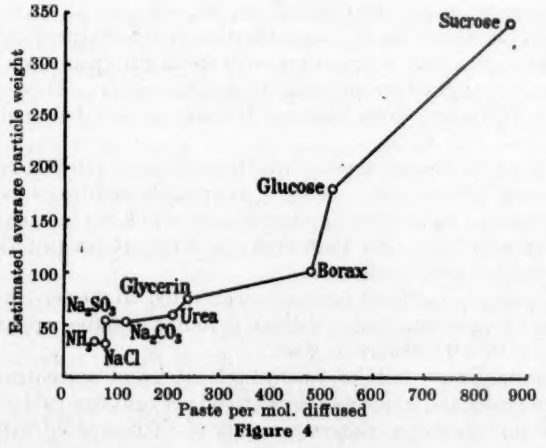

Figure 4

gradually swept down until it accumulates at the lower part near the severed ends.

The authors advance the theory that the cause of the concentration at the membrane is a bombardment of the colloid particles by the diffusing solute. The rubber particles in latex are in Brownian movement, and they migrate in cataphoresis. They must therefore be able to move freely. During dialysis there is a concentration gradient of solute from the center of the cell to the membrane, so

that the rubber particles are subjected to a greater bombardment from the inside of the cell than from the outside, and the resultant pressure will impel them towards the membrane. This pressure exerted by the solute molecules or ions is proportional to their mass, which is in agreement with the experimental result that the paste formed per solute particle diffusing is approximately proportional to the weight of the particle.

McBain and Liu[5] have noticed a somewhat similar effect in experiments on diffusion with solutions of glucose and hydrochloric acid, from which they conclude that the diffusion column of one substance by virtue of its concentration gradient may by the bombardment of its molecules accelerate, retard, or even reverse the diffusion of another substance. In this case, of course, the work dealt not with colloidal particles but with molecules and ions, so there is no concentration at the membrane, the bombarded substance being carried by the diffusing substance into the other cell, where its concentration increases.

Although McBain's results were obtained on non-colloids, there is no reason why the same effect should not occur with colloids, with the difference that the colloid will be stopped by the membrane, as we have found to occur with latex.

This theory is being investigated more fully in further work in progress in the authors' laboratories.

Concentration of Latex

From the foregoing account of the experimental work with the dialyzer, it follows that satisfactory purification is quite practicable provided dilution is allowed to a sufficient extent to prevent paste formation. It appears that all the diffusible impurities in latex are likely to cause paste formation at constant latex volume, and up to the present no simple practical means has been discovered to prevent this or to redisperse the paste. Therefore parallel experiments have been made on the concentration of the purified but diluted latex.

Two evaporative methods for the concentration of the dialyzed latex have been used in this investigation, *viz.*, evaporation with stirring from an open vessel heated on a boiling water bath, and evaporation in a spray dryer. These two methods show interesting differences both between themselves and between normal and dialyzed latex.

No difficulty was experienced in concentrating normal or purified latex by simple evaporation provided the ammonia content was maintained by periodic additions, but it is a slow process. Spray drying is much more rapid, but has the disadvantage from the experimental viewpoint that even the smallest constructional unit requires a considerable quantity of latex.

Comparing ammonia-stabilized latices concentrated to 60 per cent dry rubber content by open evaporation, dialyzed latex is found to have a relative viscosity of 0.7 compared with 5.0 for normal latex.

Comparing normal latices stabilized with Lissapol A and concentrated by evaporation in an open vessel and in a spray dryer to 60 per cent dry rubber content, the spray drying is found to give a relative viscosity of 1.9 compared with 11.0 for the open vessel.

It is not possible to compare the viscosities of normal or dialyzed latices stabilized by ammonia only and concentrated by the alternative methods, since ammonia alone will not stabilize latex sufficiently for spray drying. It is necessary to use some further stabilizer, otherwise extensive coagulation occurs during spraying. For example, 0.5 per cent of ammonium stearate on the dry rubber content of dialyzed latex will stabilize it against concentration to 62 per cent dry rubber

content, and the spray method again gives the concentrate of lower viscosity, *viz.*, 0.7 against 1.3.

The lower viscosity of the concentrates from the spray dryer is ascribed to the very much shorter heat-treatment.

The fact that dialyzed latex does not give such large viscosity differences by the two methods shows that dialysis removes some substance from latex which raises the viscosity of latex concentrates when they are prepared by a method involving relatively prolonged heating. It is not known what this substance is.

The following experiment gives further examples of this effect. Three stabilized latices were concentrated in a 500-cc. evaporator with a boiling water-jacket and stirrer from 36 per cent dry rubber content to 60 per cent dry rubber content, and their relative viscosities were measured by the falling sphere method.

Original Latex	Stabilizer Per Cent on Latex	Relative Viscosity Unstirred	Stirred
Normal	0.5 per cent Lissapol A	100	42
Dialyzed	0.5 per cent Lissapol A	2.8	2.8
Dialyzed	1 per cent K stearate and 1 per cent free KOH	1.0	1.0

It will be noted in this case that the concentrate from the dialyzed latex is again of a much lower viscosity. Moreover, the concentrate from dialyzed latex does not show thixotropy, whereas stirring of the concentrate from normal latex reduces its viscosity to about one-half its normal value.

Since the spray concentrates show an advantage in lower viscosity and speed of preparation, experiments were made on a larger spray dryer, which had been used previously to concentrate an ammonia-preserved latex, stabilized with 1 per cent of potassium stearate and 1 per cent of free caustic potash, from a dry rubber content of 38 per cent to 60 per cent. In this case it was desired to use less stabilizer, so before concentrating the dialyzed latex a preliminary run was made on normal ammonia-preserved latex. The latex was diluted to the same dry rubber content as the dialyzed latex, *viz.*, 34 per cent, and 0.5 per cent of stabilizer (Lissapol A) was added. The experiment was successful, about 60 gallons being concentrated in one hour from 34 per cent to 55 per cent dry rubber content. There was a loss of about 3–4 per cent by drying on the walls of the container.

The dialyzed latex was divided into two portions. As it is slightly less stable than normal latex, one-half was stabilized with 0.5 per cent of Lissapol A and 0.5 per cent of caustic potash. It was successfully concentrated from 34 per cent to 60 per cent dry rubber content. The second half was stabilized with 0.5 per cent of Lissapol A only, and successfully concentrated from 34 per cent to 65 per cent dry rubber content. There was in both cases a loss of about 3–4 per cent due to drying. The concentrates were of about the same fluidity as a 60 per cent centrifugally concentrated normal latex.

Although the method of spray concentration shows advantages in regard to viscosity of concentrates, it is not yet possible to take full advantage of this method, since some of the smallest drops of spray were completely dried in the process to give minute, yellow, globular particles of dry rubber. These particles do not tend to unite, and are, in fact, powder from latex in suspension in latex. They are too small to remove by straining, but can be removed experimentally by diluting the concentrate when they rise to the surface. The surface layer can be removed and the clot dried and weighed. This procedure indicates that about 17 per cent of the rubber is present in this form. The presence of these particles is apparent from the "lace-like" film of liquid latex left when a bottle of it is shaken and the latex

drawn down the shoulder or sides of the bottle. There is little doubt that a more uniform atomization of the latex in the spray would overcome these difficulties, and experiments are in hand to this effect.

The spray-dryer concentrates are perfectly stable to storage both in the presence of these large particles and after their removal.

This work has been carried out on behalf of the Rubber Producers' Research Association, to whom the authors are indebted for permission to publish.

Summary

Constructional details and methods of operation are described of a pressure dialyzer capable of treating 4 gallons of latex.

The removal by dialysis of various substances from latex maintained at constant volume is shown to cause the segregation of a concentrated, pasty layer of latex at the dialyzing membrane. A preliminary investigation of this hitherto unrecorded phenomenon indicates that the degree of paste formation is related to the molecular weight of the diffusing substance. It can be avoided by allowing some dilution of the latex to occur. It is considered that the segregation at the membrane is caused by a bombardment of the colloidal particles of rubber by the diffusing molecules of the solute, and that this effect will be of interest in many cases of diffusion through colloidal dispersions.

Concentration of ordinary and dialyzed latex by simple evaporation and by evaporation in a spray dryer is described, and dialyzed latex is shown to have an advantage in giving a concentrate of lower viscosity.

References

[1] British Patents 213,886; 243,016; 244,727; 250,639, *et seq.*

[2] British Patents 219,635; 319,410; 328,766; 393,644, *et seq.*

[3] British Patents 226,440; 268,299; 344,647, *et seq.*

[4] See also British Patents 219,277; 344,875; and 393,644. A substantially complete index with abstracts of patents dealing with the concentration and purification of latex will be found in "Rubber Latex" published by the Rubber Growers' Association, Inc

[5] *J. Am. Chem. Soc.*, **53**, 59 (1930).

[Translated for Rubber Chemistry and Technology from the Revue générale du caoutchouc, Vol. 14, No. 134, pages 19–21, September, 1937.]

Studies of the System Latex-Colloidal Clay

A. van Rossem and J. A. Plaizier

In the literature of rubber and latex, several references to studies on the use of colloidal clay in latex mixtures are to be found but, surprising as it may seem, the various purposes for which colloidal clay is employed are merely indicated, without any scientific explanation based on quantitative data being offered in a single case.* For example, colloidal clay is used for increasing the viscosity of latex, but quantitative data have not been available.

For this reason it was considered of importance to undertake a scientific and more nearly quantitative study of the latex-colloidal clay system. Some of the results of this investigation are described in the present communication which deals with experiments on the increase in viscosity brought about by colloidal clay, the diminution in tackiness of a dried latex film, the reinforcement of dried latex rubber by colloidal clay, and the flocculation of the system latex-colloidal clay.

I. Increase in the Viscosity of Latex by Addition of Colloidal Clay

It is already known that the viscosity of latex can be increased by increasing its concentration, but in various industrial applications of latex, it is undesirable to employ latex of high concentration, and for this reason it is very useful to have available a substance, like colloidal clay, which increases the viscosity.

The present authors have determined, by means of a Gorter pipette, the viscosity of latex and of latex containing colloidal clay. Mixtures containing various proportions of colloidal clay based on the rubber content were prepared, and the times of flow of these mixtures in the Gorter pipette were measured. Several kinds of colloidal clay were tested, and the results of two of the series of tests are shown in Fig. 1.

The results in Fig. 1 lead to two conclusions:

1. Colloidal clay increases considerably the viscosity of latex, the magnitude of this increase depending on the quality of the colloidal clay employed.
2. When such a mixture is allowed to stand, *e. g.*, for seventy-two hours, the viscosity increases considerably, a change undoubtedly connected in some way with the thixotropic properties of the mixture.

II. Diminution of the Adhesiveness of a Film of Dried Latex

It is a generally known fact that a film of rubber obtained by drying latex is very tacky. In some cases this property is desirable; on the other hand, in certain industrial applications of latex this peculiarity leads to difficulties. In an effort to avoid a tacky surface, colloidal clay was added to latex, and preliminary tests gave positive results. Because of this favorable outcome, quantitative tests were then carried out. Films of rubber were prepared by drying latex containing increasing proportions of colloidal clay. One side of each of these films was reinforced by cloth. Two of the dried films were stuck together by a small carriage

* See for example the following literature: Anon, *India Rubber World*, **87**, No. 6, 37 (1933); "Bentonite, Technology and Industrial Uses," American Colloid Co., Chicago, **1935**, p. 202; Hirschmann, *Rubber Age* (N. Y.), **41**, 89 (1937).

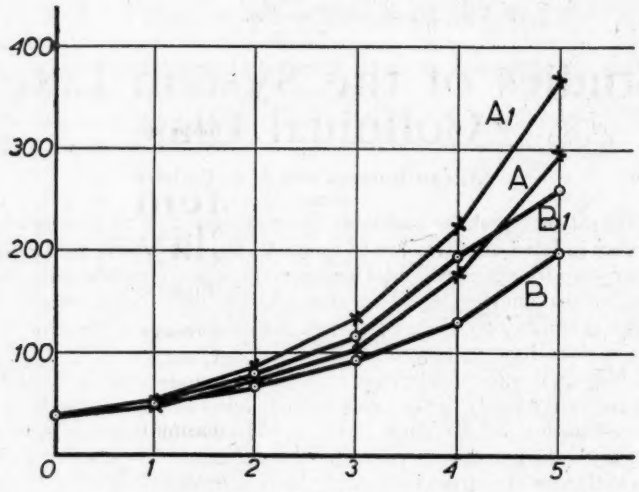

Figure 1

Increase in the viscosity of latex by addition of colloidal clay
The ordinate represents viscosity, the abscissa, percentage of colloidal clay
A mixtures with colloidal clay no. 2
A_1 the same mixtures after standing for 72 hours
B mixtures with colloidal clay no. 3
B_1 the same mixtures after standing for 72 hours

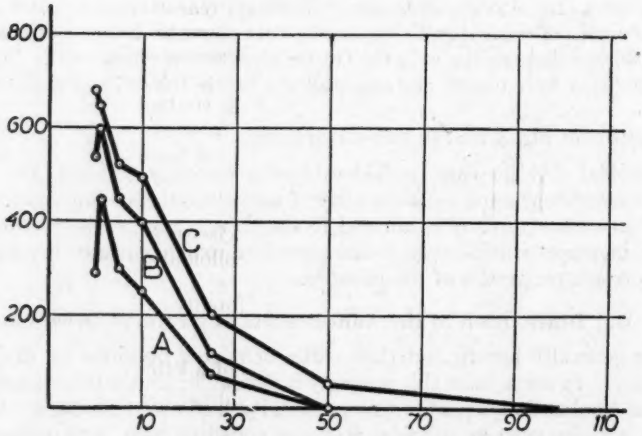

Figure 2

Diminution in the adhesiveness of a film of dried latex by addition of colloidal clay
The ordinate represents the friction in grams, the abscissa, the percentage of colloidal clay
A weight of 8.5 kg.
B weight of 23.5 kg.
C weight of 48.5 kg.

with two properly weighted rollers which rolled on the two films of rubber. The next day the force of adhesion of the two films was measured on a Schopper dynamometer by the method ordinarily employed for determining the force of adhesion between different plies of a belt. These experiments were carried out with various weights, and the results are shown in Fig. 2.

The curves in Fig. 2 seem to indicate that the addition of a very small proportion of colloidal clay increases somewhat the adhesion between the films, but with increase in the proportion of clay beyond a definite point, the adhesion diminishes rather rapidly. The pressure exerted in adhering the films also has a certain effect, as is readily understandable.

III. Colloidal Clay as a Reinforcing Filler

Latex mixtures containing progressively increasing proportions of colloidal

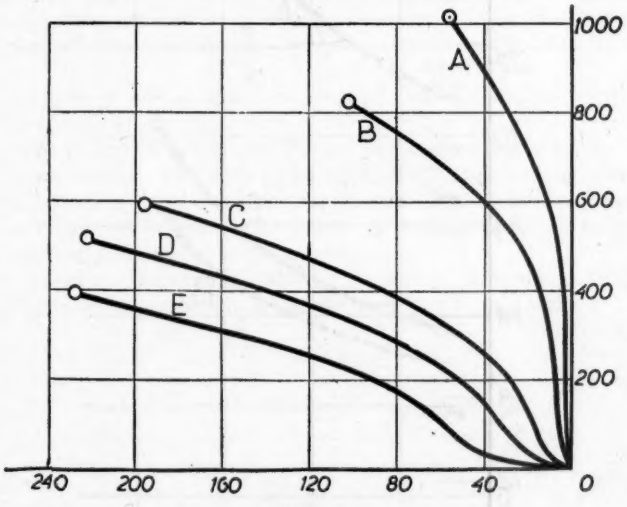

Figure 3

Colloidal clay as a reinforcing filler in rubber
The ordinate represents percentage elongation, the abscissa, stress in kg. per sq. cm.

A	No clay
B	5 parts of clay
C	10 parts of clay
D	20 parts of clay
E	30 parts of clay

clay, *viz.*, 5, 10, 20, and 30 parts of clay per 100 parts of rubber, were dried on horizontal plates of glass, and the tensile properties of the resulting films were measured on a Schopper dynamometer. The stress-strain curves are reproduced in Fig. 3.

As is evident, colloidal clay mixed with rubber in the form of latex reinforces considerably the resulting film of rubber. It is interesting then that, whereas colloidal clay mixed into crude rubber gives no reinforcement, the same material when added to latex reinforces to an extraordinary degree the dried rubber. On the contrary, carbon black has a reinforcing effect when mixed with plasticized rubber, but has no such effect in dried latex mixtures. This would lead to the conclusion that latex and colloidal clay are two hydrophilic systems, which mix much more intimately in contact with water.

IV. The Influence of Colloidal Clay on the Coagulation of Latex

When a sufficient quantity of acetic or formic acid is added to latex, coagulation takes place immediately. De Vries and Belgrave have shown in their admirable investigations that coagulation comprises two successive phenomena: (1) flocculation, an electric phenomenon, and (2) coalescence, a phenomenon of adhesion. When a certain quantity of colloidal clay is first added to latex, coagulation does not

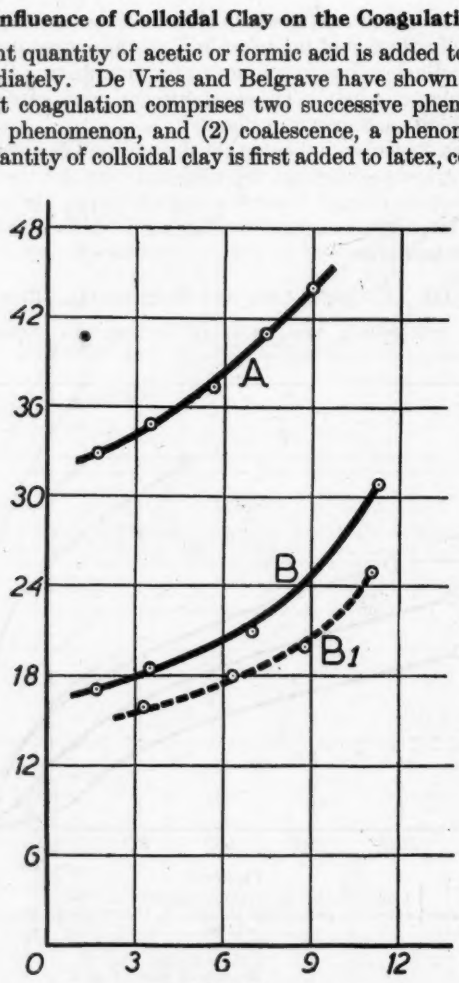

Figure 4

Flocculation of latex containing colloidal clay by addition of an acid

The ordinate represents the concentration of the latex, the abscissa, the parts of clay per 100 parts of rubber

A colloidal clay no. 1 at 20° C.
B colloidal clay no. 3 at 20° C.
C colloidal clay no. 3 at 70° C.

take place when acid is added, but only flocculation; there is in this case no coalescence. This is a very remarkable phenomenon and at the same time a very important one.

The authors have determined the minimum quantity of colloidal clay necessary to obtain a flocculate by subsequent addition of acid to latex of increasing concentration. The results of these tests are shown in Fig. 4, and lead to the following conclusions:

1. With increase in concentration of the latex, the quantity of colloidal clay required increases disproportionately rapidly
2. Different types of colloidal clay give very different results
3. Although at elevated temperatures, the quantities of colloidal clay necessary to bring about flocculation are smaller, the influence of temperature is not very important.

In conclusion, attention may be called to certain points. As for the cause of these phenomena, C. F. Vester, who has studied the subject from a colloidal point of view, is of the opinion that colloidal clay probably acts primarily as a filler. It is hoped to publish these results in another communication when experiments now in progress are finished.

During our studies it has been found that, when added to the latex-colloidal clay system, zinc oxide behaves like an acid, and flocculation takes place. This is followed, however, by slow coagulation. It is our opinion that this flocculation is probably caused by a complex zinc ion, but the phenomenon has not been studied further.

Finally, we wish to call attention to the fact that flocculation by means of colloidal clay is of very great importance in industrial applications of latex.

It is possible to add to a mixture of latex and colloidal clay all types of fillers, accelerators, and sulfur, and then to bring about flocculation by addition of an acid. This flocculate can be strained and dried. When fibrous substances are employed as fillers it is possible, with the use of a paper machine, to manufacture papers or boxes containing rubber as a component.

We have likewise succeeded by the new method in preparing a rubber powder containing fillers, for which application has been filed for a patent.

[Translated by Charles Blanc for Rubber Chemistry and Technology from Caoutchouc and Rubber (U. S. S. R.), No. 7–8, page 39, July-August, 1937.]

A New Method for the Direct Determination of Rubber

A Preliminary Communication

E. Kheraskova and E. Korsunskaya

Scientific Research Institute of the Rubber Industry, Moscow, U. S. S. R.

The conventional methods for the direct determination of rubber cannot be used for determining natural rubber in the presence of sodium-butadiene rubber. These methods are based either on precipitation of the rubber from solution or on the determination, by one method or another, of the double bonds in the rubber molecule. Since natural rubber and synthetic rubber differ in their solubilities but little, the method of precipitation obviously cannot be used for their separation. Nor are methods which involve determining the double bonds adequate to distinguish them, because both kinds of rubber are unsaturated compounds.

It was therefore of interest to develop a method of analysis based on the determination of the methyl groups, which are present only in the natural rubber molecule. Kuhn and L'Orsa (*Z. angew. Chem.*, **44**, 847 (1931)) have shown that, in the oxidation of organic compounds, a methyl group connected with a carbon atom is partially oxidized to acetic acid. The object was to develop this reaction into a method of rubber analysis by establishing the optimum conditions for the quantitative oxidation to acetic acid of all the methyl groups in the rubber hydrocarbon.

The proposed method consists in the oxidation of an acetone-extracted rubber sample with a solution of chromic acid and simultaneous steam distillation. The distilled acetic acid is then determined by titration, and the content of rubber hydrocarbon is calculated from the results of the titration.

In the oxidation of a sample of smoked sheet by this method, the resulting values for the hydrocarbon content varied from 95.3 to 96.5 per cent (according to Kemp, rubber contains 93.17 per cent of hydrocarbon). Work on improving the method and testing its applicability to the analysis of purified rubber, vulcanized rubber, and synthetic rubbers is in progress.

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Improved Packing of Rubber

Fordyce Jones

The practice of dusting smoked sheets with a suitable non-sticking powder* has now been well tested for over three years, and during that period has proved its value. Large consumers of rubber in many sections of the industry find all that is necessary is to split the bales into suitable-sized pieces ready for compounding in large mills or internal mixers without close examination.

It will be appreciated that it is somewhat difficult to make fine surgicals, inflatable or hot-water goods, toys or fancy goods, extruded or proofed goods from rubber without some form of examination. In the writer's section of the industry it is necessary that every sheet of rubber be carefully examined through the light so that it goes to the mill absolutely free from splinters, embedded bark, sand or other foreign matter, and adhered parts of any kind. The necessity of this is appreciated by all who make fine rubber ware successfully. The cost of "pulling" or separating blocks of rubber in this way is a high one; in fact, with gummy rubber, even when warm, the cost of "pulling" with labor at about 1s. 3d. an hour has been as high as $^3/_4$ d. per lb. Any way, the cost is always considerable, and as the remedy suggested herewith, and already proved in practice, costs so little and is so satisfactory it is surprising that it has not been adopted more widely.

When the idea was broached by the writer some years ago various experiments with dusting powders were made. Anything of a compounding nature is unsuitable, even in very small quantities, as no manufacturer would like to have anything in his mix unless he knew exactly what it was, and had some idea of its percentage. In the end, sample hundredweights of zinc stearate were sent out to different plantations, and three-ton consignments were regularly received. In all instances the dusted rubber practically fell out of the cases. It was unfolded into separate sheets, and could be examined in the light and passed or rejected immediately. The saving in labor was considerable, and it will be realized that with the fine powder adhering to the rubber there was little possibility of foreign matter of any kind sticking to the surface of the rubber; in fact, splinters from the case just fell off. The labor and material cost on plantations is comparatively small.

With reference to the percentage of zinc stearate in the rubber, it is so small that it is almost impossible to determine, but it is certain that by continued use of rubber treated in this way, whatever the amount is, it need not be taken into consideration in the compound. The writer would be surprised if it is as much as 0.5 per cent in the rubber. As zinc stearate has both softening and activating properties and is not objectionable in any ordinary mix, it will be seen there could be no possible objection to the use of such a small part.

It rather surprises the writer that more use has not been made of this simple process, for it is certain that such rubber should find a more ready market than some of the gummed-up blocks which are served out. It should be remembered that most raw commodities are now sold to manufacturers in improved ways. Glue is supplied in bleached and powdered forms. Shellac is sold in a variety of grades, bleached, and de-waxed. Oils and waxes are now supplied in refined and pure forms, and most of the fillers and reagents used in the rubber industry are now supplied graded and in very different forms from those used by our fathers.

* See *India-Rubber J.*, May 19, 1934.

With rubber there has been practically no development in packing since the advent of plantation rubber in pre-war days, and it might be wondered where the blame for the lack of progress with this important commodity can be laid. It is time that the suggested change be made, and it is certain that plantations treating their rubber in this way would soon find a special demand, with profit.

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The Marking of Uncured Rubber Mixes

H. J. Stern

One of the problems which confront almost every rubber manufacturer is to avoid confusion between the various qualities of mixings which he uses. Few indeed are the factories where the qualities are not so numerous and difficult to distinguish from their appearance as to provide a possible source of troublesome and costly errors. Rubbers which have received different mastication treatments and pure gum mixings are most difficult to recognize. In some cases, of course, the uncured mixings may be readily distinguished by their color. Even where this is not so, it is frequently possible to add, during the mixing process, a small quantity of coloring matter, which, though sufficient to prevent errors, is unnoticeable in the vulcanized result. This method is an excellent one, but its use is restricted to neutral tinted goods, which are not sold on color. Goods which are colored, or of a good white, and of course all black mixings, will require a different means of identification.

After a mixing has been made, it may be necessary to store it for some time before it is used. A system of storage bins or shelves, divided into sections which are labelled and reserved for the various mixings, is helpful, but by no means foolproof. Unless the greatest care is taken, mixings will find their way into the wrong compartment, and the marking or labelling of each batch is therefore an essential safeguard.

Labels and Tags

The ordinary "stick-on" label is not very satisfactory. Apart from the difficulty of adhesion, there is the possibility of the labels being torn or defaced in transit, or when slabs of rubber are stacked one on top of another. If good adhesion is obtained, the labels are difficult to remove, and may find their way into the finished goods, causing scrap. "Tie-on" labels are even less satisfactory since, except for very small batches, they are difficult to fix, and become readily detached.

A useful label, especially for small mixings, resembles that used for meat, and consists of one or more wire prongs, to which a piece of stout cord is fixed. The card may be left projecting, or arranged so that it lies flat on the rubber. For large mixings, however, even these labels have drawbacks. They may become detached, and there is the possibility of wire parts being left in the rubber, with consequent damage to warmers, calenders, and tubing machines. For these reasons, it is frequently advisable to mark each mixing by means of a suitable crayon.

Crayons

The great disadvantage of using ordinary or ready-made crayons lies in the wide variations in manufacturing conditions found in the rubber industry. In particular, variations in the temperature of the stock as it comes from the machines will be a frequent source of trouble. A crayon that will write on a slab of cold rubber may be useless at higher temperatures and, on the other hand, a crayon may be tried in the buyer's office and have an unfavorable reception, whereas on hot rubber it would behave excellently.

Crayons consist essentially of a wax or mixture of waxes mixed with pigment. The important point, so far as writing on rubber is concerned, is the melting point of the wax. Too low a melting point will lead to melting of the wax at the point of contact with the rubber, and proper writing will not be possible. This is the trouble usually encountered, and the formulas which follow will be found particularly suitable for use on carbon black mixings, where high temperatures are frequently obtained.

Mix 1

Montan wax	3 parts by weight
Beeswax	1 part by weight
Chrome yellow (lead chromate)	3 parts by weight

A high-grade chrome yellow, such as is frequently demanded in the paint trade, is not required, since only the actual full-strength color of the pigment, and not its strength in dilution, is of importance. Yellow is usually a suitable color, but other pigments may be substituted for it as required. When using other pigments due allowance must be made for differences in specific quantity, since (as in rubber mixings) it is the volume ratio which governs the final results.

Disappearing Marks

In addition to being used on rubber in slab form, it is often necessary to mark extruded or profiled lengths. The marks made by crayons from the above mix (Mix 1) will not disappear during vulcanization under ordinary conditions, and in some cases this may prove to be a drawback. If, for example, the crayons are used to mark tread rubber as it comes from the profiling machine, the finished tires will have slight yellow stains on the tread. These cannot easily be removed, and objection may be taken to them. Here, a useful type of crayon is one which gives a clear white mark on the uncured stock, but a mark that disappears entirely during cure.

Mix 2

Montan wax	3 parts by weight
Beeswax	1 part by weight
Zinc oxide	3 parts by weight
White lead	1 part by weight

The white lead must be in the form of a dry powder. This fact should be emphasized, since a linseed oil paste is frequently sold as "white lead," and such a paste is, of course, entirely unsuitable for crayon making.

Marking Wet Rubber

Yet a third type of crayon is needed to meet these cases where it is desired to write on wet rubber—for instance, where mixings are at once cooled in water or where lengths are extruded into water to avoid the danger of scorching with certain accelerators. Ordinary crayons, and also those made from Mixes 1 and 2, will not "take" on wet rubber, but by making use of the following formula these difficulties may be entirely avoided:

Mix 3

Paraffin wax (melting point 140° F.)	2 parts by weight
Tallow	1 part by weight
Chrome yellow (lead chromate)	2 parts by weight

Making Crayons

An intelligent study of these three mixes will enable the works chemist to recognize the principles which govern the compounding, and enable him to devise, where necessary, new compounds to meet special cases.

The actual manufacture of the crayons is quite a simple process, but is usually best carried out in a laboratory. The waxes are melted together in any suitable vessel, care being taken that they do not become overheated, or catch fire. The pigment is added slowly and with good stirring, and the resultant mixture poured into suitable molds. A series of cylindrical molds of any desired dimensions may be easily made in wood or metal; nevertheless, for many purposes and where only a simple marking is called for, a square crayon is quite satisfactory and is even easier to manufacture. Before filling with the mixture, the molds should be lubricated with glycerine to prevent sticking. After cooling, the molded crayons are trimmed by scraping, the scrapings, together with any broken crayons, scrap, etc., being melted in with following batch. Finally, the crayons are wrapped by rolling gummed paper around them, which serves as a protection against breakage.